Ozonation of 1,1,2,2-Tetraphenylethene Revisited: Evidence for Electron-Transfer Oxygenations(1)

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Ozonolyses of 1,1,2,2-tetraphenylethene (TPE, **1**) have been described many times in the literature, but the reports are contradictory. This reaction is particularly important for understanding the mechanism of alkene ozonolysis, in view of possible stabilization of reactive intermediates by aryl groups. Thus, systematic investigations of ozonolysis in both aprotic solvents and in protic solvents are reported here. Attention is directed to the following details that have been underestimated in the past: *i*) the actual electronic structure of ground-state ozone (O_3), *ii*) differentiation between strained and unstrained alkenes, *iii*) the significance of both the O_3 concentration and the TPE concentration, *iv*) the influence of various solvents, including pyridine, *v*) the influence of the reaction temperature, *vi*) the role of electron-transfer catalysis (ETC) and, *vii*) the effect of structural modifications. Our results suggest that ozonolysis of TPE (**1**) does not include a 1,3-dipolar reaction step, but represents a particularly interesting example of electron-donor (TPE)/electron-acceptor (O_3) redox chemistry. The present investigations include several crucial results. First, pure 3,3,6,6-tetraphenyltetroxane (**3**, m.p. 221° (dec.)) and pure tetraphenylethylene ozonide (**4**, m.p. 153° (dec.)) are prepared for the first time, although **3** and **4** have long been known. Second, the singlet diradical character of O_3, lessened by means of hypervalent-electron interaction and predicted by different calculations, is evidenced *via* reaction with the spin-trap galvinoxyl (2,6-bis(1,1-dimethylethyl)-4-{[3,5-bis(1,1-dimethylethyl)-4-oxocyclohexa-2,5-dien-1-ylidene]-methyl}phenoxy; **8**), and the zwitterionic reaction behavior of ground-state O_3 is ruled out. Third, the electron-acceptor ability of O_3 is evidenced by reactions with suitable tetraaryl ethylenes: it is enhanced by addition of catalytic amounts of protons or *Lewis* acids. Fourth, the observed distribution of the O_3 O-atoms to the two different olefinic C-atoms of the unsymmetric alkene **27b** is in full agreement with an initial single-electron transfer (SET) step, followed by a radical mono-oxygenation to cause the crucial C,C cleavage. Final dioxygenation should lead to the generally known products (ozonides, tetroxanes, hydroperoxides). The regioselectivity is found to be inconsistent with the expected decay of an intermediate primary ozonide. Finally, the treatment of 1,2-bis(4-methoxyphenyl)acenaphthylene (**36**) with O_3 (simultaneous transfer of three O-atoms) leads to the same experimental result as a stepwise transfer of one O-atom followed by a transfer of two O-atoms.

1. Introduction. – To the best of our knowledge, the first ozonolysis of 1,1,2,2-tetraphenylethene (TPE; **1**) was described in 1925 by *Fischer* and *Müller* [1]. These authors found a quantitative formation of benzophenone (**2**) upon ozonizing **1** in $CHCl_3$ at −78° (*Scheme 1*). Later experiments, carried out mostly in CCl_4 at 0°, led to formation of the tetroxane **3** as the main product (52–59% yield) [2]. But these yields were calculated on the assumption that only one molecule of peroxide could be formed from one molecule of olefin [2a]. Since the stoichiometry of tetroxane formation *via*

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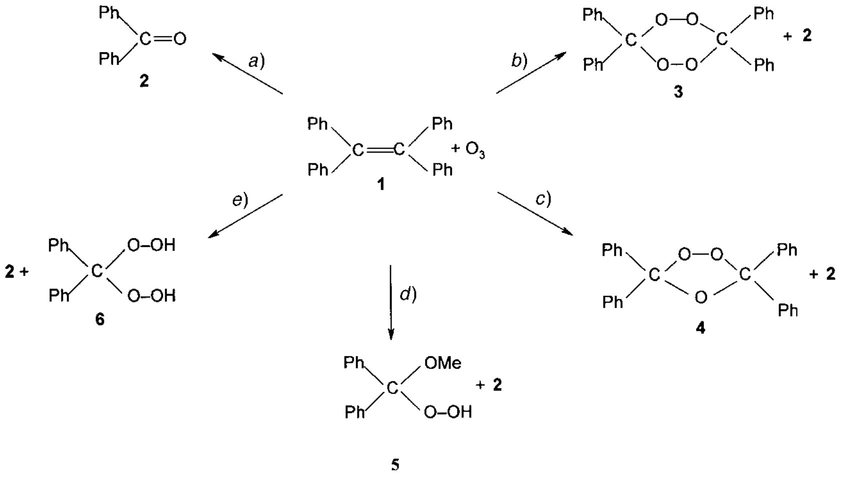
(2) Part of Ph.D. theses of *H.B.* (1988), *M.B.* (1994), *S.P.* (1992), and *C.W.* (1998), University of Saarland.

(3) Diploma thesis of *J.E.*, University of Saarland, 1994.

ozonolysis needs two molecules of olefin, these yields should be halved, and it should be recognized that benzophenone (**2**) was actually the main product. Furthermore, in 1968, *Criegee* reported that TPE (**1**) is an olefin that does not itself form an ozonide [3], and it was only three years later that he accomplished the synthesis of TPE ozonide [4], even *via* a route that had been described by others to be ineffective [2d,e]. His results were later confirmed [5], and his approach is applied here. Though the wide range of the melting points (with decomposition) described for ozonide **4** (155–169°) does not offer a criterion for the purity of samples, the difference from the reported average melting and decomposition temperatures of tetroxane **3** (200–228°) was too large to be ignored [4].

Scheme 1. *Literature Results for the Ozonolysis of TPE* (**1**)



a) $CHCl_3$, –78° [1]. *b*) CCl_4, 0° [2]. *c*) CCl_4, 0° or liquid **2**, 55° [4]. *d*) MeOH, CCl_4, 0° [6]. *e*) MeOH, $CHCl_3$, –78° [7].

Similar inconsistencies were reported for ozonolysis of TPE in the presence of MeOH. Whereas *Renard* and *Fliszár* [6][4]) reported a quantitative yield (104–120% on the basis of O_3 consumed) of diphenyl methoxymethyl hydroperoxide (**5**), *Robertson* and *Verzino* [7] described formation of diphenylmethyl dihydroperoxide (**6**) instead of **5**. *Renard* and *Fliszár* [6] did not report the isolation of hydroperoxide **5**; **5** was later prepared by another route, isolated, and characterized (m.p. 62–64°) [8], and it was proposed that formation of the established bis(hydroperoxide) **6** occurs by a reaction involving H_2O_2 [7]. Although H_2O_2 can be generated by ozonation of alcohols [9], it is known that MeOH, in particular, is not attacked by O_3 at temperatures below –20°. Even at higher temperatures, MeOH does not react with O_3 in the presence of a reactive olefin, since the olefin reacts quantitatively with O_3 faster than the O_3 can react with MeOH to form H_2O_2, or the H_2O_2 can form **6**, even in a large excess of the more nucleophilic MeOH (see *Scheme 1*).

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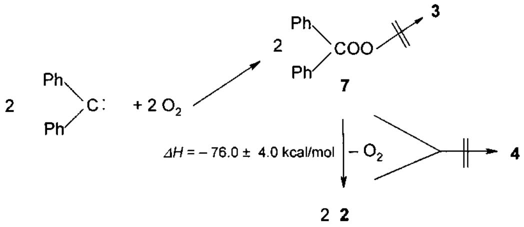
[4]) See also Table 2 in [2d].

A common proposal made by researchers who reported formation of peroxidic products **3**–**6** [2][4–7] is that ozonolysis of **1** produces the carbonyl oxide of benzophenone, **7**, as the reactive precursor. However, the only established behavior of **7** is its decomposition in matrix [10] or in solution [11] to yield benzophenone and oxygen; **3** or **4** should have been formed, at least in solution, whenever **7** or **2** were present, but were not found [11] (*Scheme 2*).

Scheme 2. *Generation and Decomposition of Benzophenone Oxide* (**7**) (in solution, according to *Griller* and co-workers [11])



From these contradictory literature reports, it seems unlikely that the ozonide **4** would form *via* the widely accepted *Criegee* mechanism [12]. The first step of the *Criegee* mechanism involves a 1,3-dipolar cycloaddition of ground-state O_3 (a known electrophile having a very modest dipole moment of 0.53 D) to the strained and distorted olefin TPE (**1**) [13], which seems highly improbable. Furthermore, **1** is known to fail the usual olefin test with Br_2 (A_E mechanism).

In view of these manifold uncertainties, we began a systematic reinvestigation of ozonations of TPE (**1**). We considered it essential to *a*) generate pure samples of **3** and **4** with reproducible melting and decomposition temperatures to use as standards in the analysis of mixtures of ozonide **4** and tetroxane **3**, *b*) determine the typical behavior of ground-state O_3 from experimental results, *c*) examine solvent, concentration, and temperature effects in TPE ozonations, and *d*) explore substituent effects for tetrasubstituted ethylenes compared to TPE ozonolyses. It seemed also prudent to optimize conditions for single-electron transfer (SET).

2. Results. – 2.1. *Preparations of Pure Tetroxane* **3** *and Ozonide* **4**. Previously reported preparations of **3** included reaction of **2** with H_2O_2 [2a], reaction of benzophenone dichloride with 30% aqueous H_2O_2 [14], ozonolysis of **1** and of other 1,1-diphenylalk-1-enes [2], and photooxygenation of diphenyl diazomethane [15]. Melting points (with decomposition) of 159–162° [8c], 170° [16], 200–220° [17], 205–206° [2d][18], 206–208° [2b], 206.5–215° [14], 212.5° [2a], 213.5–214° [15], 214–215° [19], 216–217° [2c], and 225–228° [2f] have been reported[5]. Typical properties of **3** have been described by *Marvel* and *Nichols* [14]. Because the reaction of benzophenone dichloride with 30% aqueous H_2O_2 was not always reliable [2c], we prepared only small amounts of **3** without application of O_3. It was, however, difficult to obtain a pure substance: first, minor impurities in **2** could not be removed by repeated recrystallization, and

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[5] The highest [2f] and lowest [8c] melting-point ranges reported are suspect because of inconsistencies within these citations and with the literature cited therein.

second, chromatographic separation of **3** from **2** (silica gel/CH_2Cl_2; room temperature) led inevitably to some catalytic decomposition of **3**. Cooling the chromatographic column to *ca.* 15° prevented this undesired decomposition, and in this way pure **3** was accessible (m.p. 221°, with decomposition, determined independently with a copper block and automatically recorded with a *Fus-O-mat* (*Heraeus*, D-Darmstadt)).

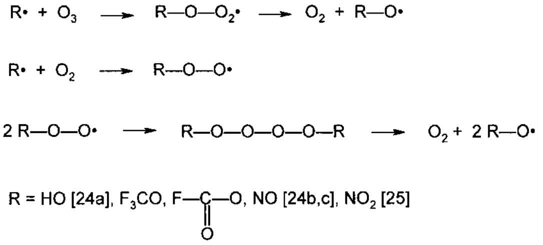
Surprisingly, samples of **3** generated by ozonolyses of TPE (**1**) and purified as described above did not have melting points in excess of 215–216°. Although the ^{1}H-NMR spectrum of a sample having a melting point of 215–216° was identical to that of one melting at 221°, the melting point of the former could not be increased by further purification. This discrepancy is probably due to the presence of a persistent trace impurity, most likely of the corresponding trimer, as indicated by mass spectroscopy (CI-MS, EE 120 eV, CH_4, 231°, 594 (0.08%).

Pure ozonide **4** was prepared according to the method of *Criegee* and *Korber* from **1** in liquid **2** at 55° [4]; pure **4** had a melting point of 153° (dec.). Although the formulae of **3** and **4** differ by only one O-atom, their ^{1}H-NMR spectra are completely different (*Fig. 1*). In particular, it should be emphasized that **3** displays a 4:4:2:6:4 pattern of aromatic-H *multiplets* at 400 MHz and a 4:6:6:4 pattern at 100 MHz [20], whereas **4** displays only two 8:12 aromatic-H *multiplets*. The lower-field 8 arom. H *multiplet* (7.37–7.44 ppm) is not superimposable on the spectrum of the tetroxane H-atoms, and can be used to calculate mutual impurities of **3** in **4**, or of **4** in **3**. Cross contamination of **3** and **4** is likely responsible for the different melting temperatures reported in literature.

2.2. *The Electronic Structure of Ground-State O_3.* The early paper by *Trambarulo et al.* [21] succeeded in establishing the view that ground-state O_3 is an allyl anion-like zwitterion (**A**, *Fig. 2*). Contemporary calculations suggest that O_3 is a singlet 1,3-diradical (**B**, *Fig. 2*) [22] or a heteroallene-like species (**C**, *Fig. 2*) with a hypervalent central O-atom [23]. Whichever the best description is, O_3 displays the typical properties of a diradical in its reactions with other radicals [24–26]. In the course of such a radical combination, one O_3 O-atom is transferred to the other radical, resulting in *mono-oxygenation* (*Scheme 3*). It has also been reported that carbon radicals react analogously with O_3 [27], but no details were given.

To probe the diradical nature of O_3, we reacted the commercially available stable organic standard radical and radical scavenger, galvinoxyl, with ozonized O_2. It was shown earlier that galvinoxyl (2,6-bis(1,1-dimethylethyl)-4-{[3,5-bis(1,1-dimethylethyl)-4-oxocyclohexa-2,5-dien-1-ylidene]methyl}phenoxy; **8**) is only relatively stable towards O_2 [28]; a solution of **8** (1.0 g, 2.37 mmol) in CCl_4 (500 ml) was reported to

Scheme 3. *Typical O-Transfer Radical Reactions of O_3 or O_2* (reactions with nitroso and nitrone spin traps [26])



$$R\cdot + O_3 \longrightarrow R{-}O{-}O_2\cdot \longrightarrow O_2 + R{-}O\cdot$$

$$R\cdot + O_2 \longrightarrow R{-}O{-}O\cdot$$

$$2\,R{-}O{-}O\cdot \longrightarrow R{-}O{-}O{-}O{-}O{-}R \longrightarrow O_2 + 2\,R{-}O\cdot$$

$$R = HO\ [24a],\ F_3CO,\ F{-}C({=}O){-}O,\ NO\ [24b,c],\ NO_2\ [25]$$

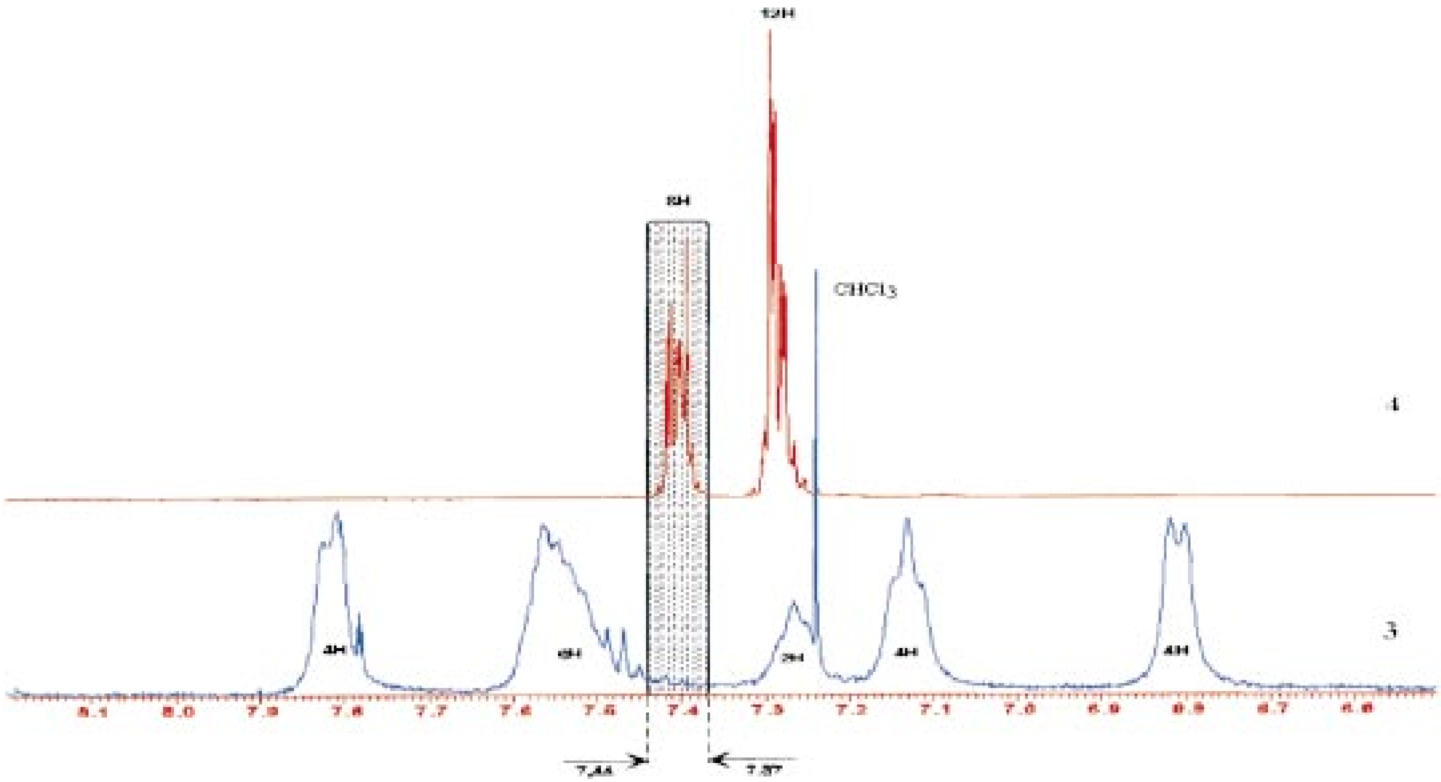


Fig. 1. *Comparison of* δ [ppm] *of 20 aromatic H-atoms of tetroxane* **3** *and ozonide* **4**

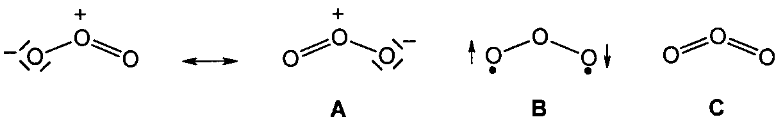


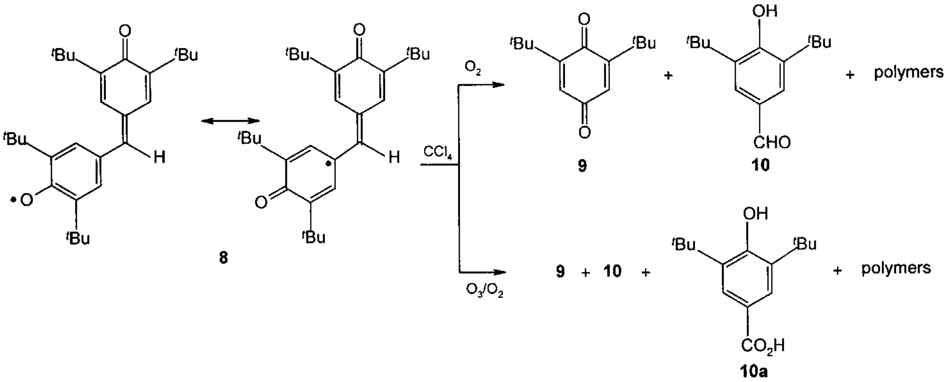
Fig. 2. *Electronic configurations of O_3 discussed in the literature* (**A** [21], **B** [22], and **C** [23])

react completely with O_2 in 24 h [28c] (*Scheme 4*). A corresponding conversion with ozonized O_2 (a stream of O_2 at 1 l/min containing 1.8 mmol O_3/min) was complete after *ca.* 4 min. Both processes resulted in formation of aldehyde **10**, which was rather stable towards O_2 alone, but could be easily converted to the substituted benzoic acid **10a** by ozonized O_2 (confirmed by an independent experiment with commercially available **10**). Polymeric impurities in both reaction mixtures were easily removed by adsorption on alumina. This result supports the proposal that O_3 is a diradical species.

To judge the contribution of the zwitterionic O_3 formula **A** (*Fig. 2*), the 'push-pull' olefin 2-(methoxymethylidene)propanedinitrile (**11**) was treated with ozonized O_2 in CH_2Cl_2 solution at temperatures between −78° and 0° [29] (*Scheme 5*). That no reaction occurred, in spite of a tenfold excess of O_3, suggests that formula **A** does not significantly contribute to the structure of O_3.

2.3. *Results of the Ozonations of TPE* (**1**) *in Aprotic Medium.* Ozonolysis of **1** in $CFCl_3$ at −105° yielded mainly **2**, and **3** in only trace amounts. Earlier ozonolyses of **1** in CCl_4 (*cf. Scheme 1*) were carried out in suspensions, since *ca.* 15 mM of **1** in CCl_4 is the solubility limit at 0° (*cf. Entry 2* in *Table 1*). Therefore, the superior solubility of **1** in CH_2Cl_2 was exploited for investigations below 0° for concentration studies, while CCl_4 was used for corresponding investigations above 0°. It was striking that the formation of ozonide **4** was observed in considerable amounts at higher reaction temperatures, and that trace amounts persisting at −78° caused depressions of the melting points of

Scheme 4. *Oxidative Cleavage of Spin-Trap Galvinoxyl* (**8**) *by O_2* [28] *or O_3/O_2*



Scheme 5. *Attempted Ozonation of Enol Ether* **11** ('push-pull' olefin)

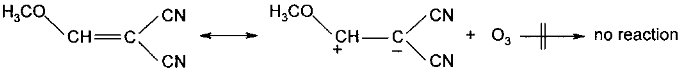


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Table 1. *Products from Ozonolysis of* **1** *in Aprotic Medium under Various Conditions*

Entry	Solvent and other conditions	Concentration of **1** [mM]	Reaction temp. [°]	Yields			
				Ketone **2** [%]	Tetroxane **3** [%]	Ozonide **4** [%]	Ester **12** [%]
1	$CFCl_3$	14	– 105	72	28	–	[a]
2	CCl_4	14	0	70	27.5	2.5	–
3	CCl_4	14	22.5	57	36	7	[a]
4	CCl_4	14	55	71.5	14	10.5	4
5	$ClCH_2CH_2Cl$	14	0	80	17	0.5	2.5
6	CH_2Cl_2	14	0	77	16	[a]	6
7	CH_2Cl_2	6	– 78	81	14	[a]	5
8	CH_2Cl_2	14	– 78	77	20	[a]	3
9	CH_2Cl_2	113	– 78	75.5	23.5	[a]	1
10	$CH_2Cl_2/FeCl_3$[b]	15	– 78	88.5	[a]	–	11.5
11	CH_2Cl_2 inverse[c]	→ 0[c]	– 78	86	–	–	14
12	CH_2Cl_2 + **2**[d]	20	0 or 22.5	quant.	–	–	–
13	CH_2Cl_2 + **2**[e]	14	0	98	2	[a]	–
14	AcOEt + **2**[f]	14	0	quant.	–	–	–
15	**2**	100	55	[g]	–	14.6	–
16	CH_2Cl_2/pyridine 1 : 2[h]	14	– 78	quant.	–	–	–

[a] Trace amounts. [b] $FeCl_3$ added as 1 ml of a 2% soln. in abs. CH_2Cl_2. [c] O_3 at 19.5 mmol/l in CH_2Cl_2 at – 78°; **1** added dropwise at 3 mmol/l. [d] 20 g of **2** in 100 ml. [e] 30 g of **2** in 150 ml. [f] 40 g of **2** in 150 ml; [g] Not determined, **2** as cosolvent. [h] Formation of pyridine *N*-oxide: *ca.* quant. yield by ^1H-NMR detection, or *ca.* 56% from conversion to the picrate (m.p. 179.5 – 180°).

isolated tetroxane **3** samples. Phenyl benzoate (**12**) was an additional impurity, formed during all reactions performed in CH_2Cl_2, and in those performed in CCl_4 above 20°. Its removal, together with **2**, from samples of **3** and **4** was easily accomplished by chromatographic purification at 15°. No discrepancies were observed for reaction performed in 1,2-dichloroethane.

The addition of a catalytic amount of anhydrous $FeCl_3$, a SET catalyst, to a solution of **1** in CH_2Cl_2 (*Entry 10* in *Table 1*) led to some surprising observations. The characteristic purple color of radical cation $\mathbf{1}^{\bullet +}$ [30] occurred only when the solvent had not been degassed (with Ar in an ultrasound bath) to remove O_2. This intense purple color likewise occurred in the presence of air after addition of strong protic acids (the intensity of the color with $CF_3SO_3H > CH_3SO_3H > H_2SO_4$) and its source, namely $\mathbf{1}^{\bullet +}$, could be characterized by ESR spectroscopy (*Fig. 3*)[6]. Surprisingly, when samples of **1** were freshly prepared by reductive methods (from benzophenone dichloride and copper [31a] or from **2** by *McMurry* reduction [31b]), the purple color changed rapidly to dark green (λ_{max} 700 nm, log ε 0.3 [32]), and the compound became ESR-inactive [33]. A similar green color was reported during oxidation of **1** with aminium radical cation salts [34]. Moreover, the purple or green color disappeared just before a molar amount of O_3 was introduced. The reactions followed the same course after consumption of equivalent amounts of O_3 (*Entry 10* in *Table 1*). The product profile from inverse ozonolysis of **1** in CH_2Cl_2 (*Entry 11* in *Table 1*) was nearly the same (*cf. Entry 10* in *Table 1*), however, the deep blue color of the O_3 solution obscured the color

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[6] Performed by *L. Eberson*, Lund, Sweden.

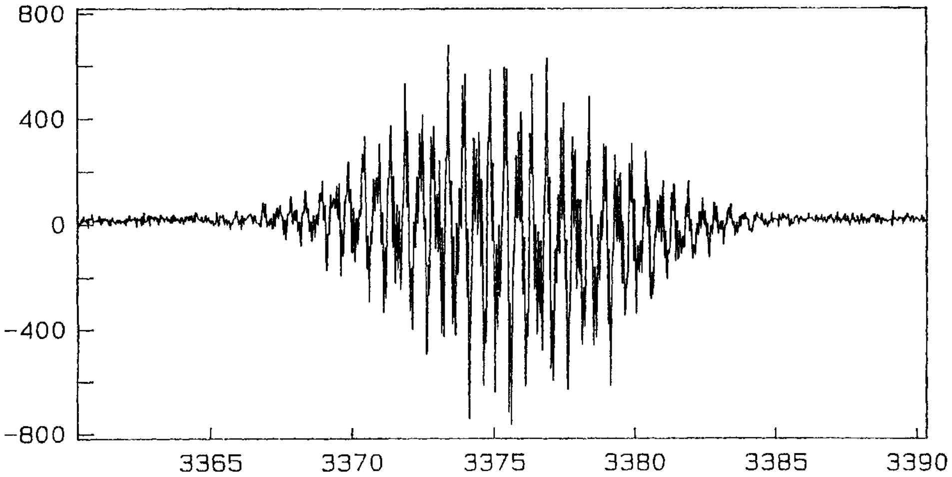

Fig. 3. *ESR Spectrum of* $\mathbf{1}^{\cdot+}$ *from* **1** *in the presence of HFP/H*$^+$*/O*$_2$

development during formation of the charge-transfer complex (*cf. Table 2*). Nevertheless, charge transfer between **1** and O_3 in a matrix experiment has been described [35].

Ozonolyses of **1** in CH_2Cl_2 or AcOEt solution in the presence of **2** led exclusively to formation of **2** (*Entries 12–14* in *Table 1*), which establishes that ozonide formation from a solution of **1** in liquid **2** at 55° (*Entry 15* in *Table 1*) was not simply the result of the usual cross-ozonolysis. The ozonide yields for *Entries 4* and *15* in *Table 1* indicate a common temperature effect (55°).

Only at best was a trace amount of ozonide **4** formed during ozonolysis at temperatures $\leq 0°$ (*Entries 1*, *5–14*, and *16* in *Table 1*). The yield of **4** from ozonolysis in CCl_4 as a function of temperature (*Entries 2–4* in *Table 1*) and the similarity in the yield of **4** under different solvent conditions at 55° (*Entries 4* and *15* in *Table 1*) points to a dependence on temperature in the formation of this product.

It is generally accepted that ozonolysis of simple olefins in the presence of pyridine does not lead to formation of pyridine *N*-oxide [36], however ozonolysis of strained olefin **1** in CH_2Cl_2/pyridine (*Entry 16* in *Table 1*) proved to be an exception in that, in addition to **2**, pyridine *N*-oxide was formed quantitatively. The pyridine *N*-oxide product was identified both by ^{1}H-NMR spectroscopy and by precipitation of its picrate (56% yield, m.p. 179.5–180° [37][7]) after evaporation of excess pyridine.

In summary, ozonolysis of TPE (**1**) in an aprotic medium is apparently dependent on solvent, concentration of **1**, reaction temperature, and on the presence of a SET catalyst.

2.4. *Application of 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) as a Radical-Cation Stabilizer. Eberson et al.* [39] provided evidence that radical cations from electron-rich arenes can be stabilized by solvation with HFP. To determine whether a similar stabilization would be observed with radical cation $\mathbf{1}^{\cdot+}$ [30], several ozonations of **1** were carried out at 0° in CH_2Cl_2 solutions containing various amounts of HFP. Whereas

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[7] A melting point of 167° recently reported [38] actually corresponds to the picrate of pyridine.

ozonation in the absence of HFP (*Table 1*) gave initially colorless to yellow solutions that ultimately decolorized, the presence of HFP in the ozonolysis solvent led to permanently yellow (HFP/**1** 4:1) to reddish brown (HFP/**1** > 20:1) solutions. This visible change was dependent on a different composition of products. Inclusion of HFP led to formation of the *Wagner-Meerwein* rearrangement product **14**, for the first time during ozonolyses of TPE. The amount of **14** formed was directly proportional to the HFP content, while the corresponding yields of **2** and of phenyl benzoate (**12**) were inversely proportional (*Figs. 4* and *5*).

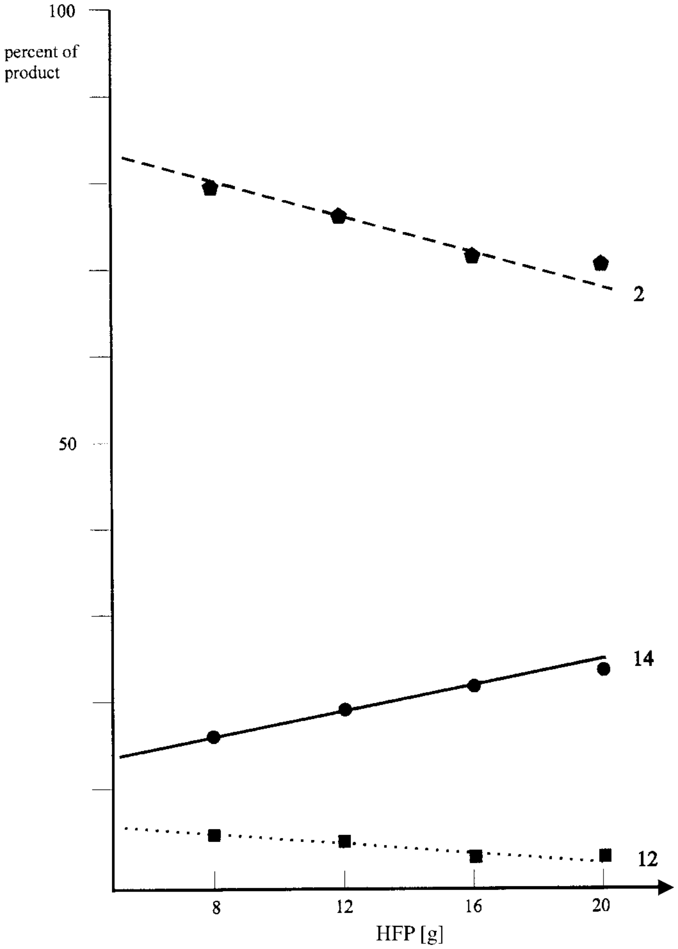
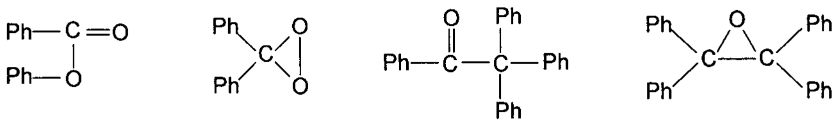


Fig. 4. *Ozonolysis of TPE* (**1**) *at 0° in* CH_2Cl_2 (20 ml) *as a function of HFP concentration*

2.5. *Oxirane Formation during Ozonolysis of* **16** *as a Substitute for* **1**. Unexpectedly, tetraphenyloxirane (**15**), corresponding to strained olefin **1**, was not found in product mixtures resulting from ozonations carried out with a mixture of O_3/O_2, although the related electron-transfer photo-oxygenation of **1** [40] generated a small amount (1.5%) of **15**, and a 3% yield of **15** from **1** was reported for an oxygenation carried out in a

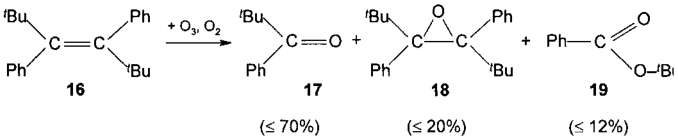


12 **13** **14** **15**

Fig. 5. *Hitherto undescribed products from ozonolyses of TPE* (**1**)

mixture of NO_2/O_2 [30b]. Hence, strained and distorted **1** was replaced by undistorted[8]) (*E*)-1,2-di(*tert*-butyl)-1,2-diphenylethylene (**16**) [41], and its ozonation products were studied for comparison [42] (*Scheme 6*). Unlike **1**, **16** was rather unreactive towards O_3, and the C,C-cleavage product, (*tert*-butyl)phenyl ketone (**17**), was the main product. Cyclic peroxides corresponding to **3** or **4** were not found, but the very unstable polymeric peroxides **20**, which had variable O contents (0.83 to 1.77 O per molecule **16** consumed), could be isolated from the solutions after ozonolysis. Each reaction furnished oxirane **18** and *tert*-butyl benzoate (**19**), no traces of the isomeric phenyl pivalate could be detected.

Scheme 6. *Products from Ozonation of* **16** *under Various Conditions*



2.6. *Ozonolysis of TPE* (**1**) *in the Presence of MeOH.* Repetition of ozonolyses of **1** in the presence of absolute MeOH, according to *Renard* and *Fliszár* [6] and to *Robertson* and *Verzino* [7], led to formation of a rather unstable hydroperoxide, which decomposed to yield **2**. Since this hydroperoxide did not display a MeO signal in its ^{1}H-NMR spectrum after careful removal of MeOH at low temperature and low pressure, the methoxy hydroperoxide **5** [6] must be ruled out. Furthermore, no dismutation of **5** to yield **6** and benzophenone dimethyl acetal had occurred. Production of benzophenone dimethyl acetal was not observed during ozonolysis or workup.

Ozonolysis of 1,1-diphenylethylene in a mixture of *t*-BuOH and 80% H_2SO_4, which has been described as a countercurrent method for the efficient ozonization of olefins, gave (*tert*-butoxy)diphenylmethyl hydroperoxide, related to the corresponding (methoxy)diphenylmethyl hydroperoxide (**5**) [2b]. We were, however, despite many attempts, unable to confirm this result.

2.7. *Ozonolyses of Different Tetraaryl Ethylenes under Various Conditions.* 2.7.1. *Tetrakis(4-methoxyphenyl)ethene* (TME; **21**). The results of ozonolyses of tetra 4-methoxy-substituted **1**, *i.e.*, **21**, either in CH_2Cl_2 or in CCl_4 under various conditions (*Scheme 7*), may be found in *Table 2*. Whereas a red-violet charge-transfer complex gradually appeared under aprotic conditions (*Entries 1–5* in *Table 2*), the expected blue color of radical cation $\mathbf{21}^{\cdot+}$ [43] instantaneously appeared in the presence of either an acid catalyst or a one-electron acceptor, when O_3 was introduced (*Entries 6–11* in *Table 2*). It is worth mentioning that no traces of ozonide **22** were found even under the

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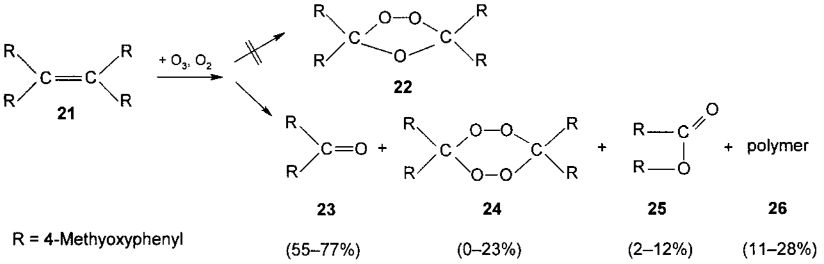
[8]) With respect to the C=C bond only.

Scheme 7. *Ozonolysis of TME* (**21**) *under Various Conditions* (see also *Table 2*)



same conditions that worked for a TPE ozonolysis (*cf. Entry 4* in *Table 1* and *Entry 12* in *Table 2*). In contrast to **1**, **21** suffered ion-radical-induced polymerization.

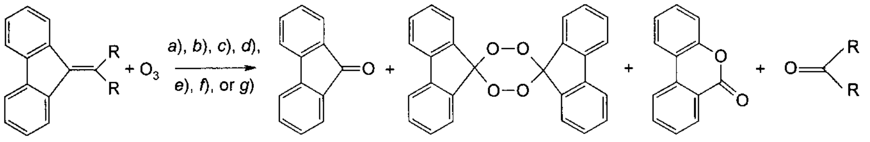
2.7.2. *9-(Diphenylmethylidene)-9*H*-fluorene* (**27a**) *and 9-[Bis(4-methoxyphenyl)-methylidene]-9*H*-fluorene* (**27b**). These unsymmetric, undistorted[8]) olefins [44] were ozonized in aprotic solvents in order to examine possible ozonide formation, or at least regioselective peroxide formation. As in the case of distorted TME, **27a**,**b** did not form ozonides, tetroxane **3**, or tetroxane **24**. Only tetroxane **29**, previously described as a product of the ozonolysis of 9,9′-bifluorenylidene (**27c**) [45], was obtained in both cases. Since ozonolysis of **27c** was reported to give dispiro[9*H*-fluorene-9,3′-[1,2]dioxetane-4′,9″-9*H*-fluorene] [46] in pinacolone as solvent, we have examined that reaction under various conditions. In aprotic solvents, **29** was isolated [45]. In contrast to the report by *Yang* and *Carr* [46a], the highest yield of tetraoxane **29** was obtained *via* ozonolysis of **27c** in pinacolone (*Scheme 8*).

Table 2. *Results of Ozonolyses* (with a dry stream of O_2/O_3 at 1 l/min (*ca.* 1.8 mmol O_3/min) until the reaction was complete, followed by dry O_2 for 15 min, and dry N_2 for 1 h at r.t.) *of TAE* (**21**) *under Various Conditions*

Entry	Solvent	Catalyst	Concentration of **21** [mM]	Reaction temp. [°]	Products and Yields[a])				Color	Time for appearance of color[b]) [min]
					Ketone **23** [%]	Tetroxane **24** [%]	Ester **25** [%]	Polymer **26** [%]		
1	CH_2Cl_2	–	4.4	– 78	69[c])	9	9	13	red-violet	2.5
2	CH_2Cl_2	–	14	– 78	69	10	8	13	red-violet	3
3	CH_2Cl_2	–	112.9	– 78	66	11	7.5	15.5	red-violet	15
4	CH_2Cl_2	–	14	0	67	7	6	20	red-violet	4
5	CCl_4	–	14	0	55	23	2	20	red-violet	5
6	CH_2Cl_2	[d])	4.4	– 78	77	–	11	12	blue	[e])
7	CH_2Cl_2	[f])	4.4	– 78	70.5	2	12.5	15	blue	[e])
8	CH_2Cl_2	[g])	4.4	– 78	77.5	–	11.5	11	blue	[e])
9	CH_2Cl_2	[h])	4.4	– 78	68.5	3.5	12.5	15.5	blue	[e])
10	CH_2Cl_2	[i])	4.4	– 78	75	–	11.5	13.5	blue	[e])
11	CH_2Cl_2	[j])	4.4	– 78	75	–	11	14	blue	[e])
12	CCl_4	–	14	55	56	10	5.5	28.5	[k])	–

[a]) Determined by ^{1}H-NMR. [b]) After introduction of O_3/O_2. [c]) Yield determined as 2,4-dinitrophenyl hydrazone 65%. [d]) 5×10^{-3} mmol CF_3SO_3H. [e]) Color change instantaneous. [f]) 5×10^{-6} mmol CF_3SO_3H. [g]) 5×10^{-3} mmol BF_3 in Et_2O. [h]) 5×10^{-6} mmol BF_3 in Et_2O. [i]) 0.24 mol $(4\text{-}BrC_6H_4)_3NSbCl_6$. [j]) Gaseous HCl. [k]) Pale yellow solution with formation of a colorless powder giving positive peroxide test; products became resinous during attempts to isolate; insoluble in $CDCl_3$.

Scheme 8. *Ozonation of 9-Alkylidene-9*H*-fluorenes* **27** *under Various Conditions*



	28	**29**	**30**	**2** or **23**
27a R = Ph	*a*) 57%	20%	trace	98%
b R = 4-Methoxyphenyl	*b*) 51%	40%	7%	88%
c R, R = [1,1'-Biphenyl]-2,2'-diyl	*c*) 49%	40%	7%	97%
	d) 67%	26%	–	
	e) 80%	14%	trace	
	f) 83%	13%	–	
	g) 88%	7%	–	

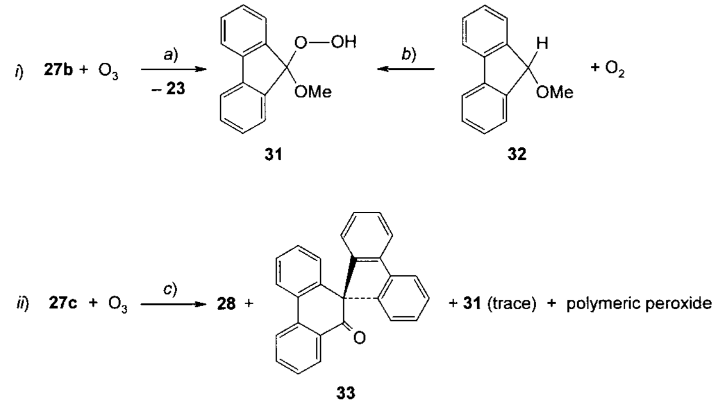
a) **27a** in CH_2Cl_2, −60°. *b*) **27b** in CCl_4, 0°. *c*) **27b** in CH_2Cl_2, −78°. *d*) **27c** in pinacolone, −50°. *e*) **27c** in CH_2Cl_2, −78°. *f*) **27c** in CCl_4, 0°. *g*) Inverse ozonolysis, addition of **27c** in CH_2Cl_2, −78°, to a solution of O_3 in CH_2Cl_2, −78°.

A marked difference was found when solutions of undistorted[8]) **27b** and of distorted[8]) **27c** were ozonized in $MeOH/CH_2Cl_2$ 1:1 at 0°: **27b** gave rise to bis(4-methoxyphenyl) ketone (**23**) and the methoxy hydroperoxide **31** [8b] in nearly quantitative yields, whereas **27c** led to a mixture of ketones **28** and **33**, with **31** present in only trace amounts (*Scheme 9*).

An independent preparation of **31** by photo-oxygenation of 9-diazofluorene in the presence of MeOH by the method of *Sawaki et al.* [8b] was possible in principle, but irradiation caused **31** to decompose nearly as quickly as it was formed. Therefore, for comparison, **31** was obtained by simple dioxygenation of 9-methoxy-9*H*-fluorene (**32**) by air in the presence of *Triton B* (*cf. Scheme 9*); the known spiro ketone **33** [34] was also independently generated.

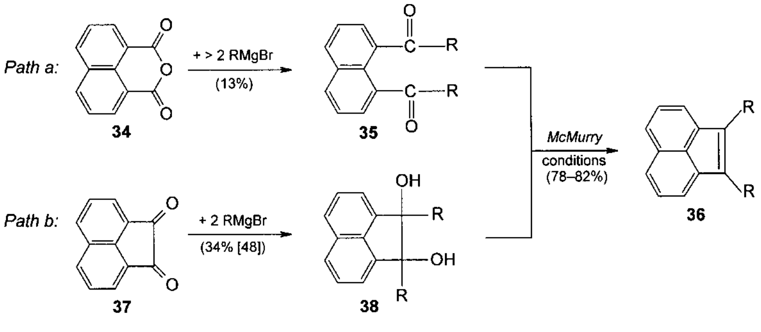
2.7.3. *1,2-Bis(4-methoxyphenyl)acenaphthylene* (**36**). Because it represents an undistorted (but *Baeyer*-strained) tetraaryl olefin possessing a rigid C-skeleton, **36** was synthesized for ozonolyses. Its ozonolysis (as a simultaneous transfer of three

Scheme 9. *Ozonation of 9-Alkylidene-9*H*-fluorenes* **27b, c** *in the Presence of MeOH*



a) $MeOH/CH_2Cl_2$ 1:1, 0°; 99%. *b*) *Triton B*, pyridine, −10°, followed by H^+; 42%. *c*) $MeOH/CH_2Cl_2$ 1:1, 0°; **28**/**33** ca. 7.5:1.

Scheme 10. *Synthetic Access to Rigid 1,2-Bis(4-methoxyphenyl)acenaphthylene* (**36**)



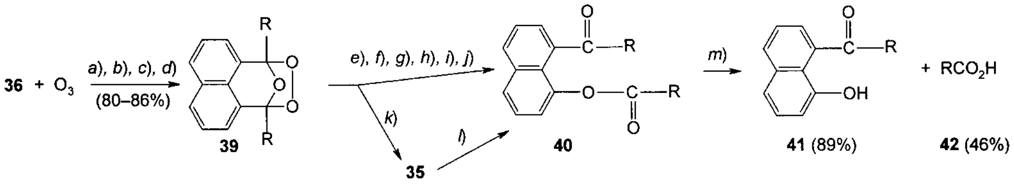
R = 4-Methoxyphenyl

O-atoms) was compared with its epoxidation, followed by C,C cleavage and final dioxygenation of the intermediate red 1,3-diyl or carbonylylide **44** (a stepwise transfer of three O-atoms; *cf. Scheme 12*), as had previously been described for the corresponding 1,2-diphenylacenaphthylene [47]. Synthesis of **36** was carried out in two ways, starting either from 1,8-naphthoic anhydride (**34**) or from acenaphthene-1,2-quinone (**37**) [48] (*Scheme 10*, *Paths a* and *b*, resp.).

Whereas ozonide **4** of TPE (**1**; an olefin with torsional strain) was formed in acceptable yields only by heating (*i.e.*, under abnormal ozonation conditions), ozonide **37** from strained **36** was formed as expected for olefins that are able to form ozonides at low temperatures (*i.e.*, under normal conditions). Moreover, ozonolysis of **36** under inverse-ozonation conditions led to essentially the same result as a normal ozonolysis (in contrast to ozonolysis of **1**, *cf. Table 1*). Whereas **3** was a rather stable ozonide, **39** was very sensitive and was decomposed by heating, by irradiation with visible light, or by acid catalysis to yield keto ester **40**. The molecular structure of **40** was confirmed by its hydrolysis to phenol **41** and 4-methoxybenzoic acid (**42**) (*Scheme 11*).

Stepwise O-transfer to **36** suffered the disadvantage that the ozonide **39** was photolabile, but the oxirane **43** must be irradiated to cause C,C cleavage to generate the intermediate **46**, which is necessary for further photodioxygenation (*Scheme 12*).

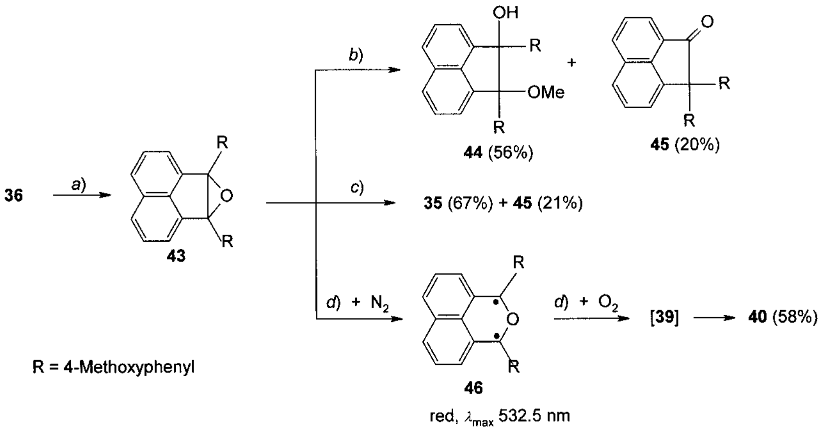
Scheme 11. *Formation and Reactions of 1,2-Bis(4-methoxyphenyl)acenaphthylene Ozonide* (**39**)



R = 4-Methoxyphenyl

a) CH_2Cl_2, −78°. *b*) CCl_4, 0°. *c*) MeOH/CH_2Cl_2 2:1, −60°. *d*) CH_2Cl_2, inverse, −78°. *e*) CCl_4, 80°, 48 h; 12% (^{1}H-NMR). *f*) Xylene, 135°, 6 d; 85%. *g*) MeOH, reflux (80°), 24 h; 40%. *h*) CS_2, r.t., 6 d; 23%. *i*) Toluene, 0°, *hν* (500-W daylight lamp), 7 h; 81%. *j*) CH_2Cl_2, 0°, cat. amount of HSO_3Cl, 1 h; 100%. *k*) Toluene, Ph_3P, 80°, 6 h; 72%. *l*) CH_2Cl_2, TFA, *m*-CPBA, r.t., 72 h; 74%. *m*) KOH/EtOH, reflux, 2 h, followed by 1M H_2SO_4.

Scheme 12. *Formation and Reactions of 1,2-Dihydro-1,2-bis(4-methoxyphenyl)acenaphthylene Epoxide* (**43**)

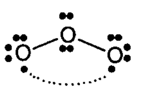


a) KHSO$_5$, acetone/CH$_2$Cl$_2$, buffer, 5–10°, 4 h; 82%. *b*) MeOH, reflux, 3 d. *c*) *m*-CPBA, NaHCO$_3$, CH$_2$Cl$_2$, r.t., 25 h. *d*) *hν*, $\lambda = 254$ nm.

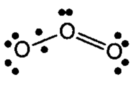
Oxirane **43** suffered exclusively heterolytic C,O cleavage in boiling MeOH (*Path b*). Olefin **36** could not be epoxidized with *m*-chloroperbenzoic acid (*m*-CPBA), because the intermediate oxirane **43** was immediately cleaved at the C–O and C–C bonds to yield a mixture of the *Wagner-Meerwein*-like rearrangement product **45** and diketone **35** (*Path c*). A selective C–C cleavage was obtained only by irradiation (*Path d*).

3. Discussion. – Pure samples of tetroxane **3** and ozonide **4** that show reproducible melting points have been generated for the first time. Hitherto reported controversial values likely reflect errors or contaminated samples. In addition, it has been established that ozonolysis of **1** in the presence of MeOH does not yield a methoxyalkyl hydroperoxide.

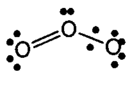
Experimental evidence indicates that ground-state O$_3$ is an open-shell singlet diradical instead of the generally accepted closed-shell zwitterion. Independent calculations by *Harcourt* [22a] led to a similar conclusion, and pointed out shortcomings in earlier calculations, specifically that the contribution of a spin-paired diradical *Lewis* structure had been largely ignored: '*Until recently, any contribution to resonance of the 'long-bond' (or spin-paired diradical) Lewis structure* A *has been largely ignored. However, it has now been calculated to be a very important structure*' and '*Considerable attention is given to the use of Pauling 3-electron bonds and increased-valence structures for providing qualitative VB descriptions of electronic structure. The increased-valence structures for electron-rich molecules – for example* B *and* C *– are equivalent to resonance between standard and long-bond Lewis structures, and usually involve Pauling 3-electron bonds as diatomic component*'.



A



B



C

The prevalence of the zwitterionic description for O_3 is perplexing given that it was excluded already 35 years ago by *Gould* and *Linnett* [49a], who concluded that the O_3 molecule is best described in terms of two three-electron bonds, rather than as a resonance hybrid of two valence bond structures each involving a single and double bond. More recent calculations also describe O_3 as a diradical species [49b][50]; O-atoms with two cumulative multiple bonds have been called 'hypervalent' [23]. *Harding* and *Goddard* [51] concluded 20 years ago that experiments describing the electrophilic nature of O_3 were misinterpreted on the basis of the assumed non-electrophilic behavior of 1,3-biradicals. However, the electrophilic nature of O-centered radical species is well-established and is consistent with the experimentally established electrophilic character of ground-state O_3; the presence of a positively charged O-atom is not required. There can be no electron delocalization in the 4π system of O_3, which possesses three parallel π-orbital axes and 1,3-diradical character with a hypervalent central O-atom having two approximately orthogonal π-systems, because these features require different molecular geometries. Important experimentally established properties of ground state O_3 include: *1*) O_3 is a peroxy radical; *2*) O_3 as a strong oxidant is an efficient one-electron acceptor; *3*) aside from O_2, O_3 is the most effective *mono*-oxygenating agent known; and *4*) although organic hydrotrioxides or trioxides (including the so-called 'primary' ozonides) have been described, they cannot result from *concerted* reactions of 1,3-diradical ozone. Ozonation reactions must involve at least two-steps, to permit energy evolution from nascent O–H or O–C bonds to the solvent and to avoid simultaneous cleavage of week O–O bonds. Since formation of trioxides was not observed in the present investigation, this property will not be further discussed (see the mechanistic investigations of *Pryor et al.* [52]).

The reaction mechanism for alkene ozonolysis proposed by *Criegee* is generally accepted, but many exceptions to the accepted mechanism of this fundamental reaction have been described. Recently, 1,3-dipolar cycloaddition of O_3 to alkenes (the first step of *Criegee*'s mechanism) has been rejected, on the basis of experimental data, in favor of an initial single-electron-transfer (SET) step to generate alkene-cation-radical/ozone-anion-radical pairs [53], in agreement with our observations. But the further conclusions of these authors follow classical ideas and are inconsistent with our observations. *1*) O_3 is a metastable compound, and its decay requires an activation energy of *ca.* 105 kJ/mol (25 kcal/mol) to yield atomic and molecular oxygen. However, its anion undergoes very rapid cleavage [54], thus successful alkene ozonolyses should be initiated by *alkene-catalyzed decomposition of* O_3[9]). The progress of the reaction depends on the structure of the alkene and on the reaction conditions (*cf. Table 1*). *2*) Most alkenes should undergo a reversible SET to O_3 as a first weakly endothermic step. However, ozonate is a reactive oxygen radical (anion) and should oxygenate alkene cation radicals very quickly and exothermally *via mono*-oxygen exchange (*Scheme 13*). Depending on the character of the alkene cation radicals, quasi-epoxidations or open-chain oxygenations can occur. However, isomeric reactive intermediates can undergo cleavage of the σ-bond *via* either exergonic isomerization [55] or β-cleavage of the

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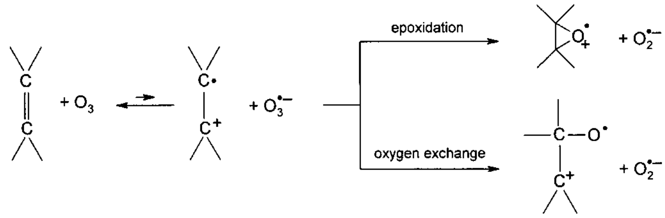
[9]) *Cf.* a) Y. A. Maletin, R. C. Cannon, *Theor. Exper. Chem.* **1998**, *34*, 57; b) P. Maslak, *Top. Curr. Chem.* **1999**, *168*, 1; c) P. Maslak, J. N. Narvaez, *Angew. Chem.* **1990**, *102*, 302; *Angew. Chem., Int. Ed.* **1990**, *29*, 283. (*added in proof*).

Scheme 13. *Fate of the π-Bond during Alkene Ozonolysis*

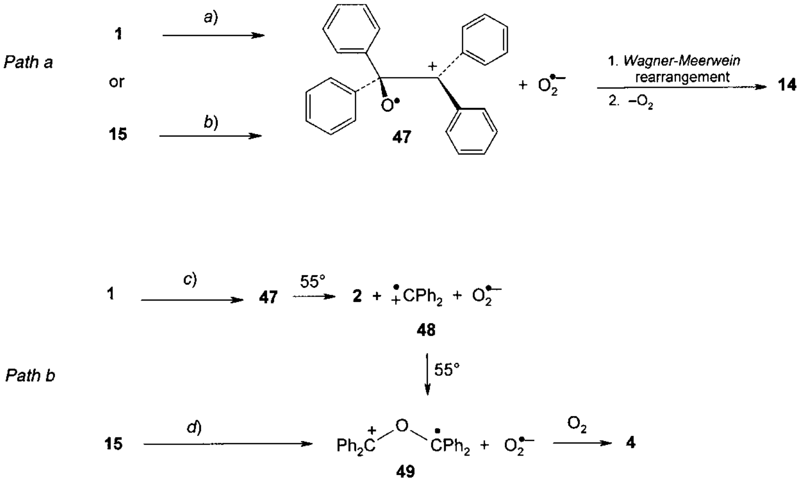


corresponding oxyl radical to generate a carbonyl compound and a carbene cation radical. The *former* situation could have occurred with the rigid cyclic alkene **36**, and represents an oxygenative ring enlargement of a strained five-membered ring to a less strained six-membered ring. Our earlier communication on cyclopentene ring ozonolyses [56] already challenged the *Criegee* mechanism. In the case of electron exchange between unsaturated hydrocarbons and O_3, it is not necessary that the initial SET be exergonic; exergonic SET is required only when stationary concentrations of free cation radicals are needed for spectral observations. If alkene cation radicals are needed only to lead to subsequent exergonic oxygenations (*cf.* formation of 1,2-dioxetanes *via Nelsen*'s CRCC oxygenation of tetraalkyl ethylene cation radicals by O_2 [57]), then they usually cannot be established for oxygenations. Nevertheless, they are required for oxygenations. Related cases have recently been discussed in the comprehensive review by *Schmittel* and *Burghart* [58a].

The *second* type of intermediate should occur with distorted alkenes like TPE (**1**) and its derivatives, where cation radicals must be a good deal more distorted than the neutral radicals. Mono-oxygenation of $\mathbf{1}^{\cdot +}$ should lead to cation radical **47**, which has been proposed as an intermediate during electron-transfer-catalyzed oxirane C–O ring cleavage of **15** induced by one-electron acceptors [59a]. Strong solvation of **47** during ozonolysis of **1** with HFP [39] favors an intramolecular *Wagner-Meerwein*-like rearrangement to yield benzpinacone (**14**; *cf. Fig. 4*). The corresponding rearrangement has been observed in the mass spectrum of **15** [59b], whereas thermal cleavage at 55° (*cf. Table 1*) should lead to **2** and the diphenyl carbene cation radical **48**. Such reactive intermediates have been studied in the gas phase [55l] as well as in solution [60] (*Scheme 14*), but these would be too reactive to be observed during ozonation. Bifunctional intermediates like **48** have been shown in kinetic studies to react as well with O_2 as with acetone (and other nucleophiles) at comparable rates [60]. These data exclude a direct proof of **48** in the present case. Therefore, unprecedented ozonide formation by thermal activation, as well as the formation of geminal bis(hydroperoxide) **6** during ozonolysis of **1** with an O_3/O_2 mixture in the presence of MeOH (*cf. Scheme 1*), follow from the assumed intermediacy of **48** *via* **51**. Auto-reaction of **48** after neutralization in the cold should react *via* **50** to give the dimer **3**, with the trimer as a trace impurity (*Scheme 15*).

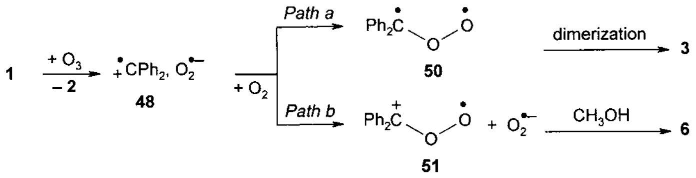
It has been found that ozonolysis of 9-[bis(4-methoxyphenyl)]methylidene-9*H*-fluorene (**27b**) in the presence of MeOH leads regioselectively to the methoxy hydroperoxide **31**, contradictory to expectation based on the *Criegee* mechanism. Ozonolysis favors hydroperoxide formation on the olefinic C-atom of the C=C double bond (*i.e.*, the carbonyl oxide C-atom), offering better stabilization of an intermediate

Scheme 14. *C–O (Path a) and C–C (Path b) Cleavage of Tetraphenyloxirane Radical-Cation Intermediates*



a) O_3, CH_2Cl_2/HFP (*cf. Fig. 4*). *b*) O_2, CH_2Cl_2, catalysis by Ph_3CSbCl_6 or by (4-Br–C_6H_4)$_3NSbCl_6$ [59a]. *c*) O_3, CCl_4, 55° (*cf. Table 1*). *d*) O_2, MeCN, *hν*, anthracene-9,10-dicarbonitrile, 1,1′-biphenyl, MeCN [5b].

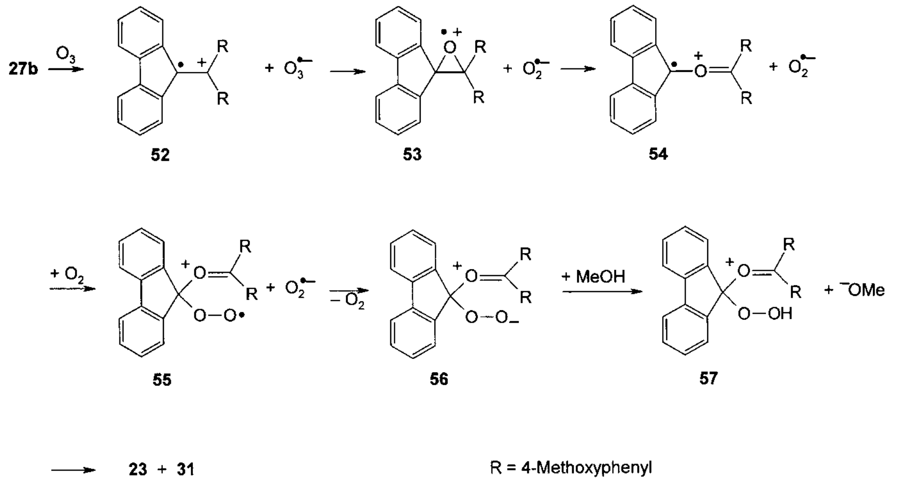
Scheme 15. *Possible Mechanism of Atypical Ozonolyses of* **1** *Involving Carbene Radical-Cation Intermediate* **48**. *Path a:* neutralization *via* nucleophile-electrophile interaction; *Path b:* dioxygenation *via* C–O radical combination.



positive charge. On the other hand, ozonation of bisfluorenylidene (**27c**) in the presence of MeOH does not form the methoxy hydroperoxide **31** (as expected), but rather **28** and the *Wagner-Meerwein*-like rearrangement product **33** (*cf. Scheme 9*). Formation of the corresponding rearrangement product **14** (*via* ozonation of **1**) required the presence of HFP (*cf. Fig. 4*). The divergent behavior of **27b** and **27c**, each containing 9*H*-fluoren-9-ylidene moieties, is ascribed to the planarity of the double-bond skeleton [44] of **27b** in contrast to the strongly distorted double bond (*cf.* its dark red color) of **27c** [13]. Consequently, only **27b** is expected to follow the proposed epoxidation path shown in *Scheme 13*, and only **27b** should form the methoxy hydroperoxide **31** during ozonolysis in the presence of MeOH through the intermediates **52**–**57** (*Scheme 16*); **27c** should follow the proposed open-chain O-exchange path leading ultimately to the *Wagner-Meerwein*-like rearrangement product **33** (similar to *Scheme 14*).

Nucleophilic substitutions at carboxonium ions (see the last step of *Scheme 16*) are well-known [61]. In the course of these reactions, carbonyl compounds (*e.g.*, **23**) serve as leaving groups.

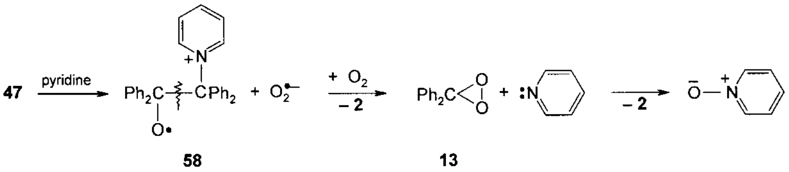
Scheme 16. *Proposed Mechanism for Formation of* **31** *by Ozonolysis of* **27b** *in the Presence of MeOH*



The mechanism of oxirane formation during alkene ozonations (*cf.* partial-cleavage products in [12b]) is uncertain. Ozone itself is proposed as the epoxidizing agent, or these are O_3-alkene reaction products, particularly dioxiranes; during ozonolysis of 2,3-dimethylbut-2-ene, formation of dimethyl dioxirane (DMDO) has been proposed as an intermediate leading to epoxide formation [62]. In the present case, an attempt to epoxidize distorted **1** with DMDO failed to yield tetraphenyloxirane (**15**). Similar behavior for diphenyldioxirane (**13**) could explain the failure to form **15** during ozonation of **1**, although the presence of the isomer of **13**, phenyl benzoate (**12**) in some experiments argues for formation of **13** as an intermediate [10]. On the other hand, in the case of '*undistorted*'[8]) alkene **16**, formation of epoxide **18** (*cf. Scheme 6*) furnished experimental proof for epoxide formation during alkene ozonation, which failed in the case of **1**.

The formation of pyridine *N*-oxide during ozonation of **1** in the presence of pyridine (*cf. Entry 16* in *Table 1*) conflicts with the usual results of the so-called 'pyridine effect' during alkene ozonolyses [63]. Whereas it was confirmed in independent experiments that ozonolysis of several other alkenes leads neither to formation of pyridine *N*-oxide from added pyridine nor to deoxygenation of added pyridine *N*-oxide during ozonations in CH_2Cl_2, distorted **1** behaved differently. In accord with the reactivity pattern of radical cations [58a], the mechanism proposed in *Scheme 17* involves initial nucleophilic attack of pyridine on the radical cation **47** during ozonolysis of **1**.

Scheme 17. *Proposed Formation of Pyridine* N-*Oxide* via *Addition of Pyridine to* **47** (*cf. Scheme 14*) *during Ozonolysis of* **1** *in the Presence of Pyridine*



Subsequent reaction steps could include radical β-cleavage of **58**, formation of **13**, and finally formation of pyridine *N*-oxide [64].

Experimental Part

1. *General.* O_3 was generated from a dry stream of O_2 at a flow rate of 1 l/min in a *Sander 301.7* laboratory ozonizer at 0.6 A, which affords O_3 at a rate of *ca.* 1.8 mmol/min as determined by iodometric titrations, For 'normal' ozonolyses, the O_3/O_2 stream was bubbled through the alkene soln.; for 'inverse' ozonolyses, abs. CH_2Cl_2 (100 ml) was first saturated with O_3 at $-78°$ by introduction of the O_3/O_2 mixture for 10 min before addition of the alkene. The O_3 content (*ca.* 5 mmol O_3) of the sat. soln. was determined by titration with 0.1M Ph_3P in abs. CH_2Cl_2 at $-78°$, until the dark blue coloration disappeared. TLC Foils *Alugram SILG/UV$_{254}$* (*Macherey-Nagel*, Germany) were used to continuously monitor the progress of the conversions. Column chromatography (CC) separations were carried out on silica gel (70–325 mesh ASTM) or on neutral alumina from *Macherey-Nagel* with a variety of columns and solvents. M.p.: a calibrated *Kofler* hot stage for instantaneous measurements that minimize depression of the m.p. caused by formation of decomposition products during the measurement (uncorrected); a *Fus-O-mat* (*Heraeus*, Germany) apparatus for fast measurements, and a classical copper block for slow measurements. UV/VIS Spectra: *Kontron Uvikon 860* spectrometer; λ_{max} in nm. IR Spectra: *Beckman IR-33* spectrometer; in cm^{-1}. NMR Spectra: *Bruker AM 400* spectrometer (in $CDCl_3$; ^1H: 400 MHz and ^{13}C: 100 MHz); δ in ppm rel. to internal Me_4Si (unless otherwise specified), J in Hz. CI-MS: CH_4, 120 eV, 220°; in m/z (rel %).

Note: All manipulations of O_3 and peroxide reaction products were carried out in an open-air laboratory behind a safety shield, and excess O_3 was destroyed with KI in dil. aq. AcOH, to minimize risk of violent decompositions or explosions. For reactions with less reactive olefins, which leave larger amounts of unreacted O_3, we recommend using solns. of sodium thiosulfate, a catalytic amount of KI, and a few drops of AcOH in H_2O to reduce residual O_3.

2. *Preparation of Tetrasubstituted Ethenes. 1,1,2,2-Tetraphenylethene* (**1**) was obtained from *Merck* and was used without further purification. Alternatively, **1** could be generated and purified starting from benzophenone dichloride and Cu powder by the reductive procedure of *Buckles* and *Matlack* [31a], or from benzophenone (**2**) by the *McMurry* procedure according to *Mukaiyama et al.* [31b]. Samples of **1** prepared by these methods were spectroscopically identical to commercially available **1**, and were suitable for ozonolytic cleavage. However, they were unsuitable for ESR spectroscopy of $\mathbf{1}^{\cdot+}$. The purple radical cation $\mathbf{1}^{\cdot+}$ could be easily prepared for ESR spectroscopy by air oxidation of commercially available **1** in the presence of $FeCl_3$ or strong protic acids (*e.g.*, conc. H_2SO_4, MsOH, or, preferably, triflic acid; *cf. Fig. 3*). Traces of transition-metal ions that survived simple recrystallizations caused a change in soln. color from ESR-active purple to ESR-inactive green (λ_{max} = 700 nm, log $\varepsilon = 0.3$). The rate of this color change varied.

*(*E*)-1,2-Di(*tert*-butyl)-1,2-diphenylethene* (**16**) was prepared according to *Leimner* and *Weyerstahl* [41a][42].

1,1,2,2-Tetrakis(4-methoxyphenyl)ethene (TME; **21**) was prepared according to the method of *Buckles* and *Womer* [65]. However, **21** readily formed stable solvates with various solvents. Thus, recrystallization from dry toluene furnished a 1:1 solvate which melted and resolidified at 174°, but after further heating displayed the lit. m.p. of 184–185°.

*9-(Diphenylmethylidene)-9*H*-fluorene* (**27a**) [66] and *9-[bis(4-methoxyphenyl)methylidene]-9*H*-fluorene* (**27b**) [44] were prepared as described.

9,9′-Bifluorenylidene (**27c**). 9-Bromo-9*H*-fluorene [67] (4.9 g, 20 mmol) was dissolved in *t*-BuOH (80 ml) at 80°, *t*-BuOK (6.7 g, 60 mmol) was added in portions with stirring, and the mixture was refluxed for 0.5 h. After cooling, the mixture was added to stirred cold 2N H_2SO_4 (150 ml). The red precipitate was filtered by suction, washed with H_2O (50 ml), and dried (P_2O_5). Recrystallization from $EtOH/CCl_4$ 1:10 furnished **27c** (4.8 g, 75%). Red crystals. M.p. 186° ([68]: 185–187°).

1,2-Bis(4-methoxyphenyl)acenaphthylene (**36**). *Path a:* Mg (1.2 g, 50 mmol) was covered with dry Et_2O (10 ml), and 1-bromo-4-methoxybenzene (9.4 g, 50 mmol) in dry Et_2O (50 ml) was added dropwise. The mixture was heated at reflux for 1 h until the metal was dissolved (after 50 min, a small amount of 1-bromo-4-methoxybenzene was added to complete the reaction). Powdered *1,8-naphthoic anhydride* (**34**; 2 g, 10 mmol) was gradually added to the cooled soln. (internal temp. 20–25°), dry benzene (20 ml) was added for better dissolution, the mixture was stirred for 0.5 h at r.t., then was heated at reflux for 12 h. After cooling, the mixture was added to a sat. aq. NH_4Cl soln.; the product was extracted with CH_2Cl_2 (50 ml), dried (Na_2SO_4), the solvent was removed *in vacuo*, and the oily residue partially crystallized at –15°. Recrystallization from acetone furnished *1,8-bis(4-methoxybenzoyl)naphthalene* (**35**) (0.5 g, 13%). Colorless crystals. M.p. 218° (215–216° [48]).

Path b: as in *Path a*, but with *acenaphthylene-1,2-quinone* (**37**) to furnish a mixture of stereoisomers of *1,2-bis(4-methoxyphenyl)-1,2-dihydroacenaphthylene-1,2-diol* (**38**) in 34% yield [48]. A *McMurry* reduction mixture was prepared by cautious dropwise addition of abs. THF (40 ml) to $TiCl_4$ (3.0 g, 15.8 mmol) in a carefully dried 3-neck flask. Dry Zn dust was added in small portions and the black mixture was heated at reflux for 1 h. A soln. of either **35** (2.0 g, 5 mmol) or **38** (2.0 g, 5 mmol) in warm abs. THF (120 ml or 40 ml, resp.) was added dropwise with stirring, and the mixture was refluxed for 14–18 h (with monitoring by TLC (silica gel; CH_2Cl_2/petroleum ether 1:1)) until **35** or **38** was consumed. The cooled mixture was added to Et_2O (200 ml), followed by cautious addition of ice water (100 ml). After the usual workup of the Et_2O layer and recrystallization from EtOH/acetone, **36** (78–82%) was obtained. Red crystals. M.p. 122°. IR (KBr): 1610 (C=C). ^{1}H-NMR ($CDCl_3$) 7.83 (*d*, *J* = 8.1, 2 H); 7.7 (*d*, *J* = 6.9, 2 H); 7.57 (*t*, *J* = 7, 2 arom. H); 7.38 (*m*, 4 arom. H); 6.91 (*m*, 4 arom. H); 3.84 (*s*, 2 MeO). ^{13}C-NMR: 158.8 (arom. C–OMe); 140.4; 137; 131.2; 128.4; 127.9; 127.8; 127; 123.5; 113.9 (arom. C); 55.2 (MeO). Anal. calc. for $C_{26}H_{20}O_2$ (364.4): C 85.69, H 5.53; found: C 86.03, H 5.48.

Note: This procedure was generally carried out with amounts of reactant ranging from 1.5–200 mmol, which afforded the indicated yields, providing that larger batches (> 200 ml solvent) were concentrated to ¼ of the original volume before workup.

3. *Preparation of Pure 3,3,6,6-Tetraphenyl-1,2,4,5-tetroxane* (**3**) *and Pure 3,3,5,5-Tetraphenyl-1,2,4-trioxolane* (**4**). Crude samples of **3**, obtained *via* the ozonolytic [2d] or non-ozonolytic [14] procedure, and **4** [4] were prepared and recrystallized as described. Since trace impurities of ketone **2** and occasionally of ester **12** could not be quantitatively removed by recrystallization, solns. of **3** or **4** were chromatographed on a water-cooled (< 15°) silica gel column. In either case, **3** or **4** was the first analyte to elute. Pure samples of **3** obtained non-ozonolytically: m.p. 221° (dec.), **3** obtained ozonolytically: m.p. 215–216° (dec.). Pure samples of **4**: m.p. 153° (dec.). Mixtures of **3** and **4** obtained by ozonolysis of **1** in CH_2Cl_2 or in CCl_4 could not be separated chromatographically; such samples of tetroxane **3**: m.p. 205–206° (dec.).

4. *Experiments to Differentiate between Singlet Diradical Character or Zwitterionic Character for Ground-State O_3.* 4.1. *Oxygenation of Galvinoxyl by O_2.* According to the procedure of *Greene* and *Adam* [28c], pure galvinoxyl (=*2,6-bis(1,1-dimethylethyl)-4-{[3,5-bis(1,1-dimethylethyl)-4-oxocyclohexa-2,5-dien-1-ylidene]methyl}phenoxy*; **8**; *ACROS Chimica*; 1.0 g, 2.37 mmol) was dissolved in dry CCl_4 (500 ml) and bubbled with a stream of dry O_2 at r.t. Decolorization was observed after 16 h, or after 6.5 h with half as much **8** dissolved in dry 1,2-dichloroethane, a slightly better solvent for dioxygen. The solvent was removed by rotatory evaporation at r.t., and a sample of the resulting viscous orange residue was dissolved in $CDCl_3$ for ^{1}H-NMR analysis: no peroxidic products were found.

4.2. *Oxygenation of Galvinoxyl by O_3/O_2.* A corresponding soln. of galvinoxyl (1.0 g, 2.37 mmol) was prepared in dry CCl_4 (500 ml) and bubbled with a stream of dry O_3/O_2 at r.t.; the O_3 content was *ca.* 1.8 mmol/min at a gas flow rate of 1 l/min. The soln. was decolorized within 4 min; galvinoxyl consumed *ca.* 3 equiv. of O_3. ^{1}H-NMR Monitoring showed formation of the corresponding principal products *2,6-di(*tert*-butyl)cyclohexa-2,5-diene-1,4-dione* (**9**), *3,5-di(*tert*-butyl)-4-hydroxybenzaldehyde* (**10**), *3,5-di(*tert*-butyl)-4-hydroxybenzoic acid* (**10a**), and a resinous polymer. The products **9** [69], **10** [70], and **10a** [71] were identified by comparison with samples synthesized independently by published methods (**9** and **10a**) or obtained commercially (**10**).

4.3. *2-(Methoxymethylidene)propanedinitrile* (**11**), prepared according to the procedure of *Jones* [72] and dissolved in dry CH_2Cl_2, did not react with even a 10-fold excess of O_3 at temps. ranging from –78° to 0° [29].

5. *Preparation of Putative Ozonolysis Products by Other Procedures. Phenyl benzoate* (**12**) [73a] and tert-*butyl benzoate* (**19**) [73b,c] were prepared by a general procedure from a soln. of PhOH or *t*-BuOH, resp., in pyridine to which was added an equimolar amount of PhCOCl: **12**, (m.p. 70°); **19**, (b.p.$_{10}$ 94–95°)10)).

Pyridine N*-oxide picrate* [37], *benzpinacone* (= *phenyl triphenylmethyl ketone*, **14**) [74], *tetraphenyloxirane* (**15**) [75], *1,1-dimethyl-3-phenylpropan-2-one* (**17**) [76], *3,3,6,6-tetrakis(4-methoxyphenyl)tetraoxane* (**24**) [77], *4-methoxyphenyl 4-methoxybenzoate* (anisyl anisoate, **25**) [78], *9,10-dihydrospiro[9*H*-fluorene-9,9′-phenanthrene]-10-one* (**33**) [79], *1,8-Bis(4-methoxybenzoyl)naphthalene* (**35**), and *1,2-Bis(4-methoxyphenyl)-1,2-dihydroacenaphthylene-1,2-diol* (**38**) [48] were prepared by published methods.

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10) A b.p.$_2$ of 96° reported in [73b] was found to be erroneous, and the b.p.$_{10}$ found here is consistent with that obtained *via* a different synthetic procedure.

*(*E*)-2,3-Di(*tert*-butyl)-2,3-diphenyloxirane* (**18**) [42]. A soln. of commercially available *m*-CPBA (2.75 g, 11 mmol, peroxide content of 70–75%) in dry $CHCl_3$ (50 ml) was added dropwise to a soln. of **16** [41a] (2.92 g, 10 mmol) in dry $CHCl_3$ at r.t. over 5 min. The mixture was stirred (20 h), an additional portion of *m*-CPBA (0.8 g, 3.3 mmol) added, and the mixture was stirred for another 3 h until **16** was consumed (TLC monitoring (silica gel; CH_2Cl_2/petroleum ether 1:1)). The mixture was diluted with Et_2O (100 ml), extracted 3 × with 10% aq. Na_2CO_3 (200 ml portions), dried ($MgSO_4$), the solvent removed, and the resulting residue recrystallized from MeOH to afford **18** (1.74 g, 56%). White crystals. M.p. 156–157°. IR (KBr): 3090, 3065, 2980, 2940, 2910, 2880, 1955, 1605, 1495, 1485, 1450, 1395, 1365, 1265, 1245, 1220, 1200, 1080, 1030, 950, 905, 885, 780, 730, 710. ^{1}H-NMR ($CDCl_3$): 7.45 (*m*, 4 arom. H); 7.29 (*m*, 6 arom. H); 0.57 (*s*, 2 *t*-Bu). ^{13}C-NMR ($CDCl_3$): 139.8; 130.9; 128.6; 127.1; 126.8; 126.0 (arom. C); 75.4 (oxiranyl C); 36.8 ($Me_3\mathit{C}$); 28.6 ($\mathit{Me_3}C$). Anal. calc. for $C_{22}H_{28}O$ (308.5): C 85.66, H 9.15, found: C 85.51, H 9.12.

*Dispiro[9*H*-fluorene-9,3′-(1,2,4,5-tetroxane)-6′,9″-[9*H*]fluorene]* (**29**). Exhaustive ozonolyses of **27c**, followed by recrystallization from dioxane, furnished **29**. M.p. (dec.) 214° [45]: (201–203°). We also prepared **29** by ozonolysis of 9-(methoxymethylidene)-9*H*-fluorene with recrystallization from dioxane: m.p. (dec.) 216° [29]. CI-MS: 393 (18.7, $[M+1]^+$), 392 (26, M^+), 377 (68, $[M+1-O]^+$), 361 (87, $[M+1-O_2]^+$), 196 (7.6, $[M/2]^+$), 180 (100, $[C_{13}H_8O]^+$), 152 (83, $[C_{12}H_8]^+$).

*Benzo[*c*]benzopyran-2-one* (**30**). Since the literature procedures [80] gave mixtures in our hands, we prepared **30** from fluorenone (**28**) by *Baeyer-Villiger* oxidation. A soln. of $(CF_3CO)_2O$ (2.1 ml, 3.15 mmol) in dry CH_2Cl_2 (5 ml) was added dropwise to a suspension of **28** (1.8 g, 10 mmol) and H_2O_2/urea 1:1 adduct (1.4 g, 15 mmol) in dry CH_2Cl_2 (50 ml). The mixture was stirred at r.t. for 48 h, a second portion of H_2O_2/urea adduct was added, and stirring was continued at r.t. for a further 72 h. The mixture was then filtered, the org. phase extracted with H_2O (50 ml), and dried ($MgSO_4$). After removal of solvent, the resulting yellow oil, which crystallized at r.t., was heated with aq. 2N NaOH (10 ml) at 80° for 10 min, filtered, and the cooled filtrate extracted with Et_2O (20 ml) to remove unreacted yellow fluorenone **28**. The aq. phase was acidified with 2N HCl and extracted 2 × with Et_2O. The usual workup furnished beige-colored crude **30** (1.5 g), which was recrystallized from petroleum ether/dry EtOH (1.1 g, 56%). Colorless crystals. M.p. 92° ([80]: 94.5°, [80b]: 93°).

*9-Methoxy-9*H*-fluoren-9-yl Hydroperoxide* (**31**). A 40% soln. of *Triton B* [81] in pyridine (0.05 ml) was diluted with pyridine (1.25 ml) and saturated with O_2 at −10°, and a soln. of *9-methoxy-9*H*-fluorene* (**32**)[11]) (1.0 g, 5.1 mmol) in dry pyridine (20 ml) was added dropwise over 95 min (with continuous bubbling of O_2 through the mixture). After warming to r.t., the mixture was buffered with one drop of glacial AcOH, diluted with ice water (150 ml), and the mixture repeatedly extracted with Et_2O. The combined org. layer was washed with 5% aq. HCl, H_2O, aq. sat. $NaHCO_3$, again with H_2O, and dried (Na_2SO_4). The ether was removed *in vacuo* without heating to yield **31**. Yellow oil; the titrated peroxide content was 27%; **31** was contaminated with unreacted **32** (43%) and fluorenone **28** (29%, as determined by ^{1}H-NMR analysis). All attempts to purify **32** led to formation of **28**.

8-(4-Methoxybenzoyl)naphthylen-1-yl 4-Methoxybenzoate (**40**). A soln. of *m*-CPBA (70–75%; 3.7 g, corresponding to 2.6g (15 mmol peracid)) in CH_2Cl_2 (30 ml) was dried ($MgSO_4$) and added to a soln. of **35** (2.3 g, 5.8 mmol) in dry CH_2Cl_2 (30 ml). The mixture was cooled to 0° and protected from light with Al foil. A soln. of TFA (0.44 ml, 5.8 mmol) in dry CH_2Cl_2 (2 ml) was added dropwise, the mixture was stirred for 48 h, a second portion of *m*-CPBA (3.7 g) in dry CH_2Cl_2 (30 ml) was added, and stirring was continued for another 48 h. This procedure was repeated for another 48 h, until **35** was completely consumed (TLC monitoring, silica gel; CH_2Cl_2). Subsequently, the soln. was filtered and the liquid phase washed with 10% aq. Na_2SO_3, sat. aq. $NaHCO_3$, 2 × with H_2O, and dried ($MgSO_4$). After removal of the solvent *in vacuo*, the resulting brownish oil crystallized on stirring with a mixture of Et_2O (3 ml) and acetone (10 ml). Recrystallization (AcOEt), and additional chromatographic purification of the mother liquor afforded **40** (1.76 g, 74%). M.p. 134–136°. IR (KBr): 1735 (OC=O), 1670 (C=O). ^{1}H-NMR ($CDCl_3$): 8.0 (*d*, $J = 8.3$, 1 H); 7.85 (*d*, $J = 8$, 1 H); 7.72 (*m*, 2 H); 7.55 (*m*, 2 H); 7.39 (*m*, 3 H); 7.29 (*m*, 1 H); 6.83 (*m*, 2 H); 6.6 (*d*, $J_{AB} = 9.1$, 2 H); 3.89 (*s*, MeO); 3.77 (*s*, MeO). ^{13}C-NMR ($CDCl_3$): 196.3 (C=O); 164.3 (OC=O); 163.9; 163.6 (arom. CO); 146.0; 135.7; 135.3; 132.5; 132.2; 130.1; 129.4; 126.2; 125.7; 125.4; 124.7; 121.5; 120.6; 113.4; 113.1 (arom. C); 55.5; 55.4 (MeO). Anal. calc. for $C_{26}H_{20}O_5$ (412.5): C 75.72, H4.89; found: C 75.70, H 4.74.

8-(4-Methoxybenzoyl)naphthalen-1-ol (**41**). A mixture of **40** (0.7 g, 1.7 mmol) and KOH (0.2 g, 3.4 mmol) in EtOH (25 ml) was heated under reflux for 2 h. The volume was reduced by evaporation to *ca.* 10 ml. The

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[11] Attempts to synthesize **31** *via* the Li salt were unsuccessful and led to oxidative dimerization; 9-methoxy-9*H*-fluorene is known [82a] and was prepared according to [82b].

mixture was added to ice-water (80 ml) and acidified with 1M H_2SO_4. The aq. phase was extracted 3 × with AcOEt (30 ml), the resulting org. phase was washed with H_2O, dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The resulting yellowish crystalline mixture of **41** and *4-methoxybenzoic acid* (**42**) was separated by CC (silica gel, AcOEt). The first fraction yielded **41** (0.4 g, 89%), which was recrystallized from AcOEt. Colorless crystals. M.p. 148–150°. IR (KBr): 3150 (OH), 1655 (C=O). ^{1}H-NMR ($CDCl_3$): 8.05 (*dd*, $^1J = 8$, $^2J = 1.3$, 1 H); 7.85 (*d*, $J = 8.3$, 2 H); 7.53 (*m*, 2 H); 7.44 (*m*, 2 H); 7.05 (*d*, $J = 8.4$, 1 H); 6.96 (*d*, $J_{AB} = 8.3$, 2 H); 3.88 (*s*, MeO); 1.6 (br. *s*, OH). ^{13}C-NMR ($CDCl_3$): 200.7 (C=O); 163.8 (arom. *C*–OMe); 152.5 (arom. C–OH); 135.7; 134.9; 133.1; 131.9; 131.4; 129.1; 127.3; 124.2; 122.2; 121.3; 113.6 (arom. C); 55.6 (MeO). Anal. calc. for $C_{18}H_{14}O_3$ (278.3): C 77.68, H 5.07; found: C 77.80, H 5.19.

4-Methoxybenzoic acid (**42**) (0.12 g, 46%), obtained from the second fraction, was identical to an authentic sample.

1,2-Bis(4-methoxyphenyl)-1,2-epoxy-1,2-dihydroacenaphthylene (**43**). A mixture of $KHSO_5$ (caroate; 10 g, corresponding to 30 mmol $KHSO_5$) and $NaHCO_3$ (13 g, 154 mmol) in distilled H_2O (100 ml) and 0.002M aq. Na_2(EDTA) (20 ml) was vigorously stirred at 5° while a soln. of **36** (4.2 g, 13.8 mmol) and 18-crown-6 (0.2 g, 0.07 mmol) in CH_2Cl_2 (80 ml) and acetone (15 ml) was added dropwise. After stirring for 4 h at 5–10°, **36** was consumed (TLC monitoring) and the mixture was poured into ice-cold H_2O. Separation of the org. phase and usual workup afforded a yellow oil that crystallized from Et_2O/petroleum ether on cooling: **43** (1.56 g, 82%). Colorless crystals. M.p. 138–139°. UV (CH_2Cl_2): 285 (10230). ^{1}H-NMR ($CDCl_3$): 7.85 (*d*, $J = 8.2$, 2 H); 7.53 (*t*, $J = 8.1$, 2 H); 7.46 (*d*, $J = 7.2$, 2 H); 7.39 (*d*, $J_{AB} = 8.2$, 4 H); 6.85 (*d*, $J_{AB} = 8.6$, 4 H); 3.77 (*s*, 2 MeO). ^{13}C-NMR ($CDCl_3$): 159.3; 141.7; 138.1; 132.5; 129.2; 127.3; 126.2; 124.7; 123.0; 113.5 (arom. C); 76.0 (C–O–C); 55.2 (MeO). Anal. calc. for $C_{26}H_{20}O_3$ (380.5): C 82.08, H 5.3; found: C 82.02, H 5.43.

1,2-Bis(4-methoxyphenyl)-2-methoxy-1,2-dihydroacenaphthylen-1-ol (**44**). Oxirane **43** (0.2 g, 0.52 mmol) was refluxed in abs. MeOH (20 ml) until complete methanolysis was observed by TLC (*ca.* 3 d). The solvent was removed *in vacuo*, and the resulting viscous yellow-brown oil was chromatographed (silica gel; CH_2Cl_2). The *Wagner-Meerwein* rearrangement product *2,2-bis(4-methoxyphenyl)-1,2-dihydroacenaphthylen-1-one* (**45**) [48] was collected in the first fraction (40 mg, 20%). The second fraction contained **44**, which was crystallized from AcOEt (110 mg, 56%). Colorless crystals. M.p. 205–206°. IR (KBr): 3470 (OH). ^{1}H-NMR ($CDCl_3$): 7.89 (*d*, $J = 8.3$, 1 H); 7.83 (*d*, $J = 8.2$, 1 H); 7.61 (*m*, 2 H); 7.44 (*d*, $J = 6.8$, 1 H); 7.34 (*d*, $J = 7$, 1 H); 7.05 (*d*, $J = 8.8$, 2 H); 6.64 (*d*, $J = 8.8$, 2 H); 6.33 (*s*, 4 H); 4.93 (*s*, OH); 3.72 (*s*, MeO); 3.57 (*s*, MeO); 3.07 (*s*, MeO). ^{13}C-NMR ($CDCl_3$): 158.8; 157.9 (arom. *C*–OMe); 146.9; 139.3; 138.0; 135.9; 131.0; 129.7; 129.4; 129.0; 128.1; 127.9; 126.9; 125.7; 124.4; 123.5; 121.3; 113.7; 112.9; 112.2 (arom. C); 93.1 (*C*–OMe); 90.6 (C–OH); 55.1; 55.0; 52.1 (MeO). Anal. calc. for $C_{27}H_{24}O_4$ (412.5): C 78.62, H 5.86; found: C 78.38, H 5.76.

6. *Photooxygenation of* **43**. Oxirane **43** (0.38 g, 1 mmol) was dissolved in dry toluene (100 ml), degassed with ultrasound under N_2, and irradiated (500-W Hg high-pressure lamp) under N_2 at r.t. After 10 min, a few ml of the intensely red soln. was transferred to a dry Ar-filled UV cell, and an absorption with λ_{max} 532.5 nm was recorded. Dry O_2 was bubbled through the remainder of the irradiated soln., which became instantaneously decolorized. Complete conversion of **43** after 10 h was indicated by TLC (alumina, toluene/AcOEt 10:1). The solvent was removed *in vacuo*, and the remaining yellow-brown oil was crystallized from Et_2O/MeOH, affording **40** (0.24 g, 58%).

7. *Oxidation of Alkene* **36** *by* m-*CPBA*. A mixture of **36** (0.6 g, 1.64 mmol), CH_2Cl_2 (50 ml), sat. aq. $NaHCO_3$ (50 ml), and *m*-CPBA (70–75%, 0.3 g, ca. 1.8 mmol) was stirred for 24 h at r.t. Another portion of *m*-CPBA (0.3 g) was added and stirring continued for 1 h until **36** was completely consumed (TLC monitoring), and the mixture was worked up. Instead of epoxide **43**, rearranged ketone **45** (0.13 g, 21%, m.p. 151° (acetone) [48]), and the C–C cleavage product **35** (0.43 g, 67%, m.p. 218° (acetone) [48]), were isolated by CC (silica gel, CH_2Cl_2) in the first and the second fractions, resp.

8. *General Ozonation Procedures.* 8.1. *Tetraarylethylenes* (TPE, **1**: *Table 1* and *Fig. 4*; TAE, **21**: *Table 2*; 9-alkylidene-9*H*-fluorenes, **27a**,**b**,**c**: *Scheme 8*; and **36**: *Scheme 11*). Routine ozonolyses were carried out under normal conditions, *i.e.*, introduction of a dry stream of O_2/O_3 (*ca.* 3%) at a flow rate of 1 l/min (corresponding to *ca.* 1.8 mmol O_3/min) into a soln. of the alkene. When the reaction was complete, dry O_2 was bubbled through the mixture for further 15 min at the reaction temp., and dry N_2 was bubbled through the mixture for 1 h at r.t. before the mixture was worked up (see *Table 2* for details regarding catalysts, quantities, concentrations, solvents, and reaction temp.). The following procedures from *Schemes 8* and *11* were selected as typical examples of ozonolyses of **27c** and of **36**. Olefin **27c** (1.0 g, 3 mmol) in dry 3,3-dimethylbutan-2-one (pinacolone, 50 ml) was ozonized at –50° until the red color disappeared. The solvent was removed *in vacuo*, and the remaining yellow-white residue was stirred with MeOH (5 ml), stored for 12 h at 0°, and filtered by suction. The resulting crystals were suspended in MeOH (3 ml), heated to reflux, the hot suspension was

filtered, and the product recrystallized from dioxane to yield **29** (0.25 g, 21%). Colorless crystals. M.p. 214° (203° [45][80b]). Workup of the mother liquor of the hot suspension in MeOH yielded additional **29** (60 mg, for a total yield of 0.31 g, 26%) together with fluorenone **28** (0.72 g, 67%, m.p. 83° (EtOH)). Refluxing **29** in PhCl did not lead to chemiluminescence as reported by *Yang* and *Carr* [46a]. Because of the $>10°$ deviation from literature values [45][80b] for the m.p. of **29**, this product was further characterized by spectroscopic methods. IR (KBr): 3020, 1615, 1590, 1455, 1315, 1225, 1210, 1160, 1030, 1000, 760. ^{1}H-NMR ((D_6)DMSO): 7.98 (*d*, $J = 7.7$, 4 H); 7.81 (*d*, $J = 7.7$, 2 H); 7.52 (*m*, 8 H); 7.39 (*t*, $J = 7.4$, 2 H); 6.87 (*m*, 2 H). ^{13}C-NMR ((D_6)DMSO): 135.5; 129.4; 123.6; 121.1 (arom. C); 95.4 (O–C–O). CI-MS: 393.3 (18.7 $[M+1]^+$), 392.3 (26, M^+), 377.3 (68.3, $[M+1-O]^+$), 361.3 (87.4 $[M+1-O_2]^+$), 180.2 (100, $[C_{13}H_8O]^+$), 152.2 (83.1 $[C_{12}H_8]^+$).

8.2. *1,2-Bis(4-methoxyphenyl)acenaphthylene Ozonide* (**39**).Olefin **36** (2.0 g, 5.5 mmol) in dry CH_2Cl_2 (150 ml) was ozonized at $-75°$ until the red-orange color had disappeared, followed by workup according to the general procedure to yield **39** (1.95 g, 86%), which could be recrystallized from warm (but not refluxing) MeOH. Nearly white crystals. M.p. 161°. IR (KBr): 3060, 3020, 2980, 2940, 2905, 2850, 1620, 1585, 1520, 1500, 1470, 1440, 1355, 1305, 1280, 1255, 1180, 1090, 1075, 1050, 1030, 1005, 830, 790. ^{1}H-NMR ($CDCl_3$): 7.83 (*m*, 2 H); 7.65 (*m*, 4 H); 7.37 (*m*, 2 H); 6.99 (*m*, 6 H); 3.85 (*s*, 2 MeO). ^{13}C-NMR ($CDCl_3$): 160.5 (arom. C–OMe); 135.8, 132.9; 128.4; 128.3; 125.7; 125.5; 123.4; 113.7 (arom. C); 110.0 (ozonide C); 55.4 (MeO). Anal. calc. for $C_{26}H_{20}O_5$ (412.5): C 75.72, H 4.89; found: C 75.73, H 5.01.

9. *Generation of 8-(4-Methoxybenzoyl)naphthalen-1-yl 4-Methoxybenzoate* (**40**) *from Ozonide* **39**. 9.1. *Photo-catalyzed Rearrangement*. Ozonide **39** (0.5 g, 1.2 mmol) in abs. toluene (100 ml) was irradiated, under N_2 at 0°, with a 500-W halogen day-light lamp (7 h). After storing the mixture for several days at $-20°$, crystalline **40** was obtained in nearly quant. yield. Recrystallization from AcOEt yielded colorless product (0.4 g, 81%), which was identical to the product from peracid oxidation of diketone **35**.

9.2. *Acid-Catalyzed Rearrangement*. To a stirred soln. of **39** (0.2 g, 0.5 mmol) in abs. CH_2Cl_2 (20 ml) under N_2, one drop of HSO_3Cl was added at 0°. The colorless soln. immediately became reddish brown. TLC analysis (silica gel; CH_2Cl_2/petroleum ether 1:1) revealed quant. isomerization of **39** to keto ester **40**. After 1 h, the soln. was extracted with sat. aq. $NaHCO_3$, followed by H_2O, then dried ($MgSO_4$), and the solvent was removed *in vacuo*, yielding homogeneous **40** in quant. yield (TLC).

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