

Ozonolysis of Allenes and Alkylidenecyclopropanes (Homoallenes)

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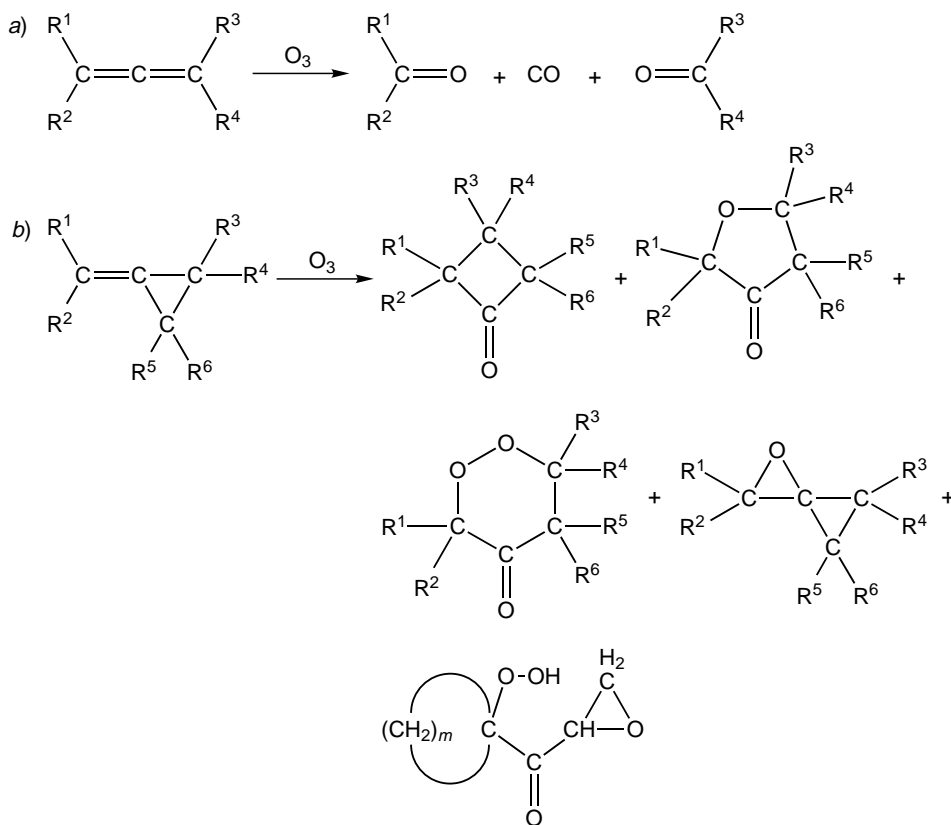
Allenyl methyl ether (**1**) and (diphenylmethylene)cyclopropane (**5**) were ozonized with an ozone/oxygen mixture. Formation of the observed products cannot be satisfactorily rationalized *via* the familiar modified *Criegee* mechanism. However, a single-electron transfer (SET) mechanism provides a simple rationale.

1. Introduction. – *Bailey* [1] has included known allene ozonolyses in a chapter on ‘Special Liquid Phase Ozonolyses’ because they do not follow the classical scheme exactly. Whereas the so-called ‘*Kolsaker* route’ [2] with simple allenes leads to two carbonyl compounds and CO (*Scheme 1,a*), sterically hindered allenes form different nonperoxidic products. Similar unexpected results have been observed in the ozonolyses of alkylidenecyclopropanes, *i.e.* *Feist*’s ester [3a], and cycloalkylidenecyclopropanes [3b,c], even though they are not sterically hindered (*Scheme 1,b*). Moreover, both nonperoxidic and peroxidic products have been found in these cases.

A good case has been made for the position that ground-state ozone is best viewed as a singlet biradical rather than as a 1,3 dipole or a resonance-stabilized zwitterion [4]. Ozone reactions, particularly with electron-rich species, can be understood as redox reactions because the role of ozone as a strong oxidant is incontestable. A comparison of the classical and an alternative (single-electron transfer = SET) mechanism for the ozonolysis of alkenes is outlined in *Scheme 2*.

Hitherto, rationalizing the results of allene or alkylidenecyclopropane ozonolyses (*cf.* *Scheme 1* [1–3]) required that the *Criegee* mechanism be supplemented with additional hypotheses. An example that includes both an allene and an alkylidenecyclopropane system was first investigated by *Hartzler* [5] (*Scheme 3*). This reaction has been reinvestigated by *Crandall* and *Schuster* [6][7] in the course of a general study of the mechanism for allene ozonolyses. The results in *Scheme 3* show that the absence of steric hindrance does not guarantee that ozonolyses will follow *Kolsaker*’s route. *Crandall* and *Schuster* concluded that this reaction ‘is found to be a general transformation that proceeds by a nonobvious pathway’. Consequently, this example should be a challenge for our alternative (SET) mechanism (*cf.* *Sect. 3*). The alternative (SET) mechanism (*Scheme 2*) demands the formation of an intimate pair of radical ions resulting from initial electron transfer by the unsaturated hydrocarbon to the ozone. Suitably substituted allenes and alkylidenecyclopropanes should be interesting species in terms of the regioselective formation of radical cations. Thus, in this paper, the results of ozonations of allenyl methyl ether (**1**) and (diphenylmethylene)cyclopropane (**5**) in aprotic solvents are described.

Scheme 1. Ozonation Products from a) Substituted Allenes and from b) Substituted Alkylidenecyclopropanes



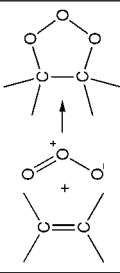
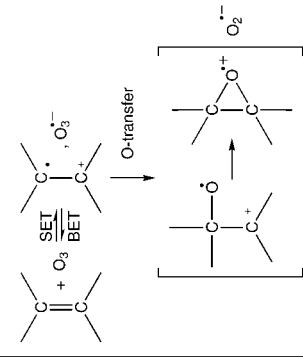
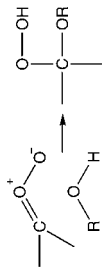
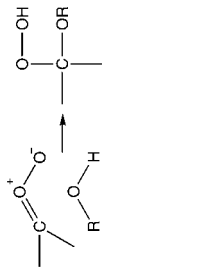
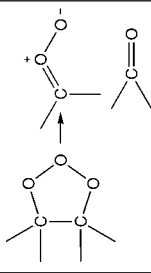
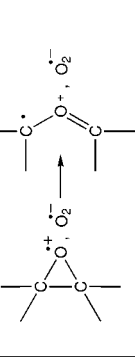
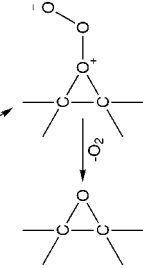
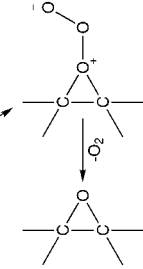
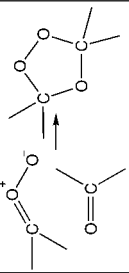
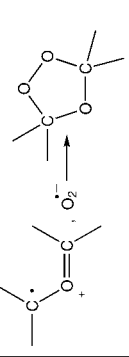
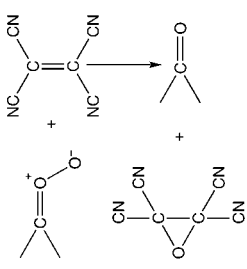
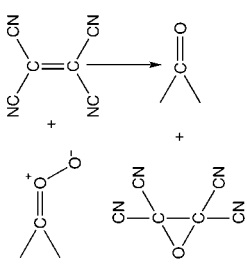
Supposition: C(R³,R⁴) migrates better
than C(R⁵,R⁶)

for $m = 3,4,5$ and $R^3-R^6 = H$

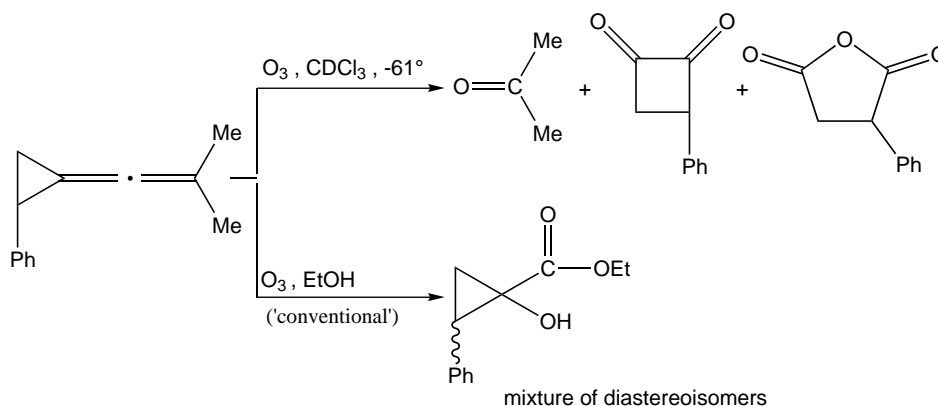
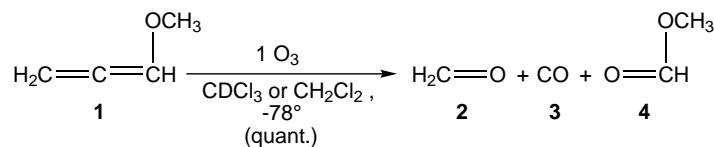
2. Results. – *Ozonolyses of 1 and 5.* Ozonolysis of ether **1** followed *Kolsaker's* route to yield **2–4** (Scheme 4). Neither partial cleavage products nor peroxidic products formed. This conversion has been exploited as a general method to convert allenyl to formyl substituents [8]. In the present case, reductive workup with Et₃N in ⁱPrOH [8] was unnecessary.

Ozonolysis of (diphenylmethylene)cyclopropane (**5**) in CHCl₃ has been reported long ago [9]. Benzophenone (**6**) was the only product identified. Our preparation of the starting alkene **5** by elimination reactions starting from cyclopropyldiphenylmethanol proved to be disappointing from (cyclopropyldiphenylmethyl)pyridinium iodide, in the final step, only (3.6%) of **5** were obtained). Synthesis of **5** by modified *Wittig* carbonyl olefinations of benzophenone [10] have been reported to afford **5** in high yields, *i.e.* 80% by *Route A* starting from (3-bromopropyl)triphenylphosphonium bromide, and 75% by *Route B* starting from cyclopropyltriphenylphosphonium bromide. We were

Scheme 2. Comparison of the Classical (Criegee) and of the Alternative (see [4]) Ozonolytic Cleavage of C=C Bonds

a) Cleavage of the π -moiety	 <p>Classical pathway</p>	 <p>Alternative pathway</p>	c) Formation of ether hydroperoxides	 <p>Classical pathway</p>	 <p>Alternative pathway</p>
b) Cleavage of the σ -moiety	 <p>Classical pathway</p>	 <p>Alternative pathway</p>	d) Direct formation of oxiranes	 <p>Classical pathway</p>	 <p>Alternative pathway</p>
c) Formation of ozonides	 <p>Classical pathway</p>	 <p>Alternative pathway</p>	e) Indirect formation of oxirane-tetracarboxitrile	 <p>Classical pathway</p>	 <p>Alternative pathway</p>

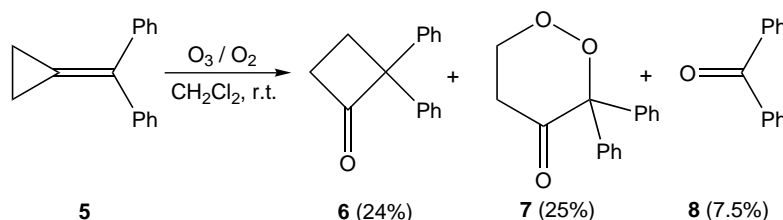
Scheme 3. Results of Allenylidencyclopropane Ozonolysis According to Crandall and Schulter [6][7]

Scheme 4. Ozonolytic Fragmentation of Allenyl Methyl Ether (**1**)

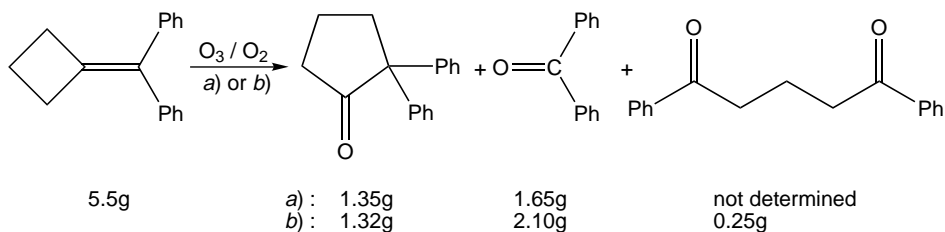
able to confirm the formation of **5** by these routes in both our labs, but our yields were much lower (*ca.* 35% by *Route A* and < 10% by *Route B*). Two difficulties encountered in the synthesis by *Route B* should be mentioned. *a*) Although the bottle of cyclopropyltriphenylphosphonium bromide (*ACROS Chemicals*) bore no warning that it was a hydrate, a sample of 25 g lost *ca.* 10% of its weight when it was stored in a desiccator over diphosphorus pentoxide. When this H₂O was not carefully removed, the final workup gave mainly crystalline cyclopropyldiphenyl – phosphin oxide (m.p. 133° [11]). *b*) Even when the H₂O was removed, the clear reaction mixture from the *Wittig* olefination of benzophenone instantaneously became turbid and dark brown, when traces of air entered during workup. The resulting dark brown resinous product (described in [9]) gave a poor yield of **5** after chromatographic purification. Once purified, **5** remained unchanged over a half year (under dry air).

(Diphenylmethylene)cyclopropane **5** was ozonized in CH₂Cl₂ at room temperature under normal conditions, and the reaction products **6**–**8** were isolated by chromatography (*Scheme 5*). In analogy to *Scheme 1,b*, the oxidative ring-expanded product 2,2-diphenylcyclobutanone (**6**) and the cyclic peroxy ketone 3,3-diphenyl-1,2-dioxan-4 one (**7**) were isolated. A small amount of benzophenone (**8**) was also isolated and assumed to be a regular ozonolysis product.

In this connection, it seems reasonable to point to the results of the ozonolysis of the homologous (diphenylmethylene)cyclobutane [12], which affords both the ring-expanded product 2,2-diphenylcyclopentanone and 1,5-diphenylpentane-1,5-dione (*Scheme 6*).

Scheme 5. Ozonation Products of (Diphenylmethylene)cyclopropane (**5**) in CH_2Cl_2 at Room Temperature

Scheme 6. Ozonation Products of (Diphenylmethylene)cyclobutane According to Graham and Williams [12]

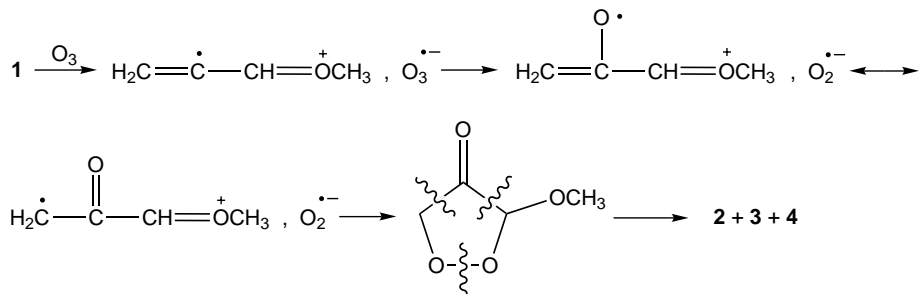


a): Dry AcOEt (100ml) at -10° . b): (25ml) and $\text{BF}_3 \cdot \text{OEt}_2$ (3ml).

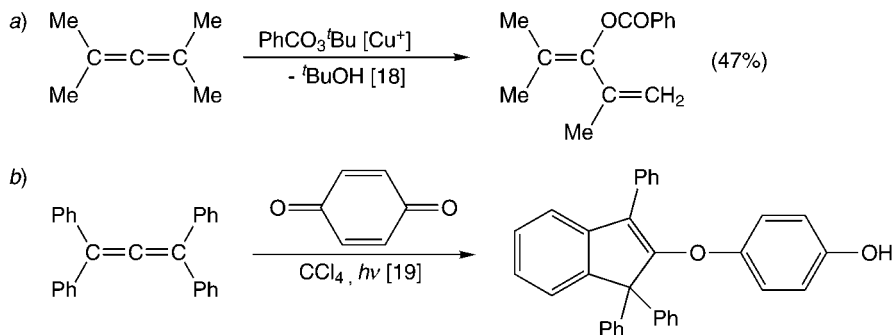
Attempted preparation of (diphenylmethylene)cyclobutane from cyclobutyldiphenylmethanol [12][13] revealed similar difficulties as encountered in the synthesis of **5** (see above). Heating in the presence of HCOOH [13] furnished the isomeric ring-expanded product 1,2-diphenylcyclopentene. A systematic investigation of substituted methylenecyclobutane ozonolyses has been carried out by *de Boer* and co-workers [14] who found anomalous outcomes that were substituent-dependent.

3. Discussion. – Ketene *O*-oxides have been invoked as intermediates in the ozonolysis of allenes [1][2][6] to rationalize the formation of *carbon monoxide*. Our electron-transfer scheme offers a different explanation. Ozonolysis of allenyl ether **1** proceeds readily (see *Scheme 7*). It is well-known that 1,2-dioxolan-4-ones formed from cyclopentadienones and $^1\text{O}_2$ cannot be trapped because they decompose *in situ* to yield two carbonyl groups and CO (1,2-dioxolan-4-ones as intermediates in singlet-oxygen cycloadditions [15a–h] and in fluoride-ion-catalyzed singlet-oxygen cycloadditions [15i]). As shown by *Frimer et al.* [16], these oxidative decarbonylations are often caused by peroxide anions that produce the corresponding intermediates, too. With regard to the oxygenation of the central allene sp C-atom, note that allenes are valence tautomers of cyclopropylidene carbenes (*cf.* the so-called cyclopropylidene-allene rearrangement), and carbenes react readily with oxygen.

On the other hand, it was reported that the ground state of a *cyclic* allene possesses a central C-atom having singlet diradical character [17]. Consequently, acyloxylation of tetramethylallene (with *tert*-butyl perbenzoate under copper(I) catalysis) occurred at

Scheme 7. Alternative Explanation of Kolsaker's Route [1][2][6] of the Ozonolytic Fragmentation of Sterically Unhindered Allenes such as **1**

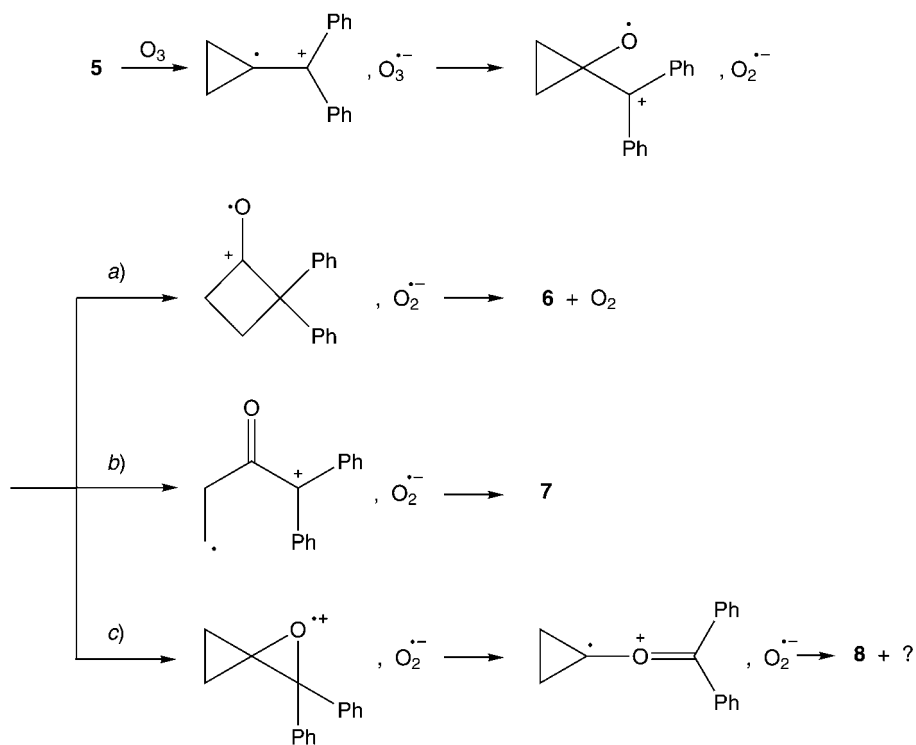
the central C-atom [18]. Similar O-attack was observed upon irradiation of tetraphenylallene and 1,4-benzoquinone [19] (Scheme 8).

Scheme 8. Oxygenations of Allenic Systems at the Central *sp* C-Atom

We assumed that the MeO group would regioselectively stabilize the positive charge of **1**⁺, and that a corresponding effect would be exerted by the two Ph groups of **5** (Scheme 9). We note that Paths *a* and *b* in Scheme 9 correspond to normal rearrangements for cyclopropylmethyl cations. The opposite regioselectivity for the distribution of the structure units in **5**⁺ would have cleaved the CH₂CH₂ moiety between the two CH₂ groups *via* disrotatory ring opening. However, both **6** and **7** contain the original CH₂CH₂ unit, in full accord with the formation of 2,2-diphenylcyclopentanone (Scheme 6) and in analogy to the formation of **6** in Scheme 5.

Crandall and Schuster [6] explained their results (*cf.* Scheme 3) with the classical Criegee scheme. An electron-transfer proposal could also easily rationalize their results.

Redox chemistry, *i.e.* electron-transfer reactions and radical chemistry, is the basis of life in terms of air oxidation of organic materials. Metastable ozone, a product from the photoexcitation of molecular oxygen, is better viewed as a particularly strong oxidant rather than as a 1,3-dipole. Hence, ozonolyses are related to photochemical reactions. Therefore, the results of this experimental work are more readily rationalized in electron-transfer terms than in terms of the more familiar 1,3 dipole cycloaddition framework.

Scheme 9. Redox Pathway During Ozonation of Alkylidenecyclopropane **5**

a) 1,2-Migration.

b) β -Cleavage.

c) C-O Ring closure with subsequent C-C cleavage and elimination of benzophenone as nucleofuge

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 Fischer 503 laboratory ozonizer affording O_3 at a rate of ca. 2 mmol/min for the ozonation of **1** and in a Welshbach t-23 ozonizer for the ozonation of **5**. Anal. TLC: silica-gel plates, 0.25-mm thick; fluorescent indicator. Qualitative determination of CO was carried out with Dräger-10/a carbon monoxide tubes. M.p.: Heraeus Fus-O-mat or Gallenkamp-MFB-595 digital apparatus; uncorrected. IR Spectra: Beckman IR-33 or -4230 and Perkin-Elmer 710b spectrometer; in cm^{-1} . NMR Spectra: Bruker AM-400 spectrometer; 1H at 400 and ^{13}C at 100 MHz; in $CDCl_3$; alternative ^{13}C measurements, Nicolet 360 N.B.; δ in ppm rel. to internal Me_4Si , J in Hz. MS: Kratos MS-80-GC/MS; INCOS data system, which gives medium-resolution data; m/z (rel. %). Combustion analyses were done by Desert Analytics, Tucson, Arizona.

2. *Starting Materials.* The 1-methoxypropa-1,2-diene (**1**) was easily prepared from methyl prop-2-ynyl ether by isomerization with potassium $t-BuO$ [20], and (diphenylmethylene)cyclopropane (=1,1'-(cyclopropylidene)methylene)bis[benzene]; **5**) was obtained in poor yields according to [10].

3. *Ozonolysis of 1-Methoxypropa-1,2-diene (1).* A soln. of **1** (1.4 g, 20 mmol) in dry CH_2Cl_2 (50 ml) was ozonized at -78° for 10 min. An equimolar amount of ozone was consumed by **1**, whereupon the colorless soln. turned blue. Effluent gases were passed through a Dräger 10/a carbon monoxide tube, which indicated the formation of carbon monoxide (**3**) during the ozonolysis. Evaporation to dryness yielded 0.37 g (62%) of

paraformaldehyde (polymeric **2**) exhibiting a dec. temp. of 136° (commercial polymeric formaldehyde (*Merck*): dec. between 120 and 170°). Additional CH₂O escaped with the effluent gas stream during the ozonolysis. IR (KBr): 3460, 3000, 2950, 1240, 1130, 1095, 990 [21].

Volatile methyl formate (**4**) was established as a reaction product by means of a second ozonolysis run with **1** (0.7 g, 10 mmol) in CDCl₃ (10 ml). Direct measurement of the resulting soln. revealed spectra identical to those of an independent sample of **4** in CDCl₃. IR (CDCl₃): 2980, 1725, 1210, 1165, 910, 730. ¹H-NMR (CDCl₃): 3.8 (s, MeO); 8.1 (s, HCO₂Me). Compounds **2–4** were the only observed products.

4. *Ozonolysis of (Diphenylmethylene)cyclopropane (5)*. The ozonator was flushed with O₂ for 1 h. A soln. of **5** (0.5 g, 2.4 mmol) in CH₂Cl₂ (20 ml) was ozonized at r.t. CH₂Cl₂ was added, as necessary, to maintain the solvent level. Upon completion of the ozonolysis, the solvent was evaporated, and the residue chromatographed (silica gel (70 g), CCl₄/petroleum ether 1:1 (10 100-ml fractions), then CCl₄ (10 100-ml fractions) followed by CHCl₃ (100-ml fractions). *Frs. 13–16* afforded 2,2-diphenylcyclobutanone (**6**; 0.13 g, 24%), identical (IR, ¹H-NMR, MS) to authentic material prepared by oxidation of **5** with 3-chloroperbenzoic acid [22]. IR (CHCl₃): 1770. ¹H-NMR (CDCl₃): 2.76 (t, CH₂); 3.10 (t, 2 CH₂); 7.33 (br. s, 10 arom. H). MS: 222 (9.6, M⁺), 180 (100).

Frs. 18–20 afforded benzophenone (0.03 g, 7.5%).

Frs. 22–25 yielded crystalline 3,3-diphenyl-1,2-dioxan-4-one (**7**; 0.152 g, 24.5%). M.p. 97.8–99.4°. IR CHCl₃: 1725. ¹H-NMR (CDCl₃): 2.85 (t, CH₂); 4.78 (t, CH₂); 7.27 (m, 5 arom. H); 7.37 (m, 5 arom. H). MS: 210 (41), 77 (100). Anal. calc. for C₁₆H₁₄O₃; C 75.6, H 5.5; found: C 76.0, H 5.6.

Peroxy ketone **7** gave a positive test with *N,N*-dimethyl-*p*-phenylenediamine hydrochloride (= *N,N*-dimethylbenzene-1,4-diamine hydrochloride), which supports the conclusion that **7** has a peroxide moiety [23].

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