The History of Ozone

Part III[1])

C. D. Harries and the Introduction of Ozone into Organic Chemistry

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This paper is dedicated to *Jack D. Dunitz* on the occasion of his 80th birthday; may he have many more in good health. *D. G.* described *Jack* as '*the wisest man I know*'.

The introduction of ozone into organic chemistry is due to the work of *C. D. Harries*, first in Berlin but mainly in Kiel, during the period 1903–1916. He established experimental procedures for ozonolysis, demonstrated the generality of the reaction of unsaturated compounds with ozone, and showed that ozone could be used for the synthesis of a variety of sensitive compounds. Most important for the future development of organic chemistry, he established that ozonolysis could be an important tool for determining the structures of organic compounds. He also initiated investigations into the mechanism of ozone reactions with alkenes, which culminated about forty years later in the *Criegee* mechanism for ozonolysis.

Introduction. – The important role that ozone (O_3) has played in structural organic chemistry was summarized by *Bentley* [2] in 1972: '*The reaction of ozone with double bonds, followed by the decomposition of the resulting products, is one of the most-reliable procedures for oxidative fission of unsaturated molecules and for determining the precise location of the unsaturation.*' At that time, it was rare to find an organic chemistry laboratory in the United States that did not sport the dark blue ozone generator manufactured by the (now apparently defunct) *Ozone Products Division* of the *Welsbach Corp.* Ozone has also been a useful synthetic reagent and presented chemists with a challenging mechanistic puzzle.

In 1847, *C. F. Schönbein*, the discoverer of O_3 [1a], made the important observation [3] that, unlike inorganic compounds, organic compounds were not converted to the highest possible oxidation states of the component elements (CO_2, H_2O, *etc.*) by O_3 but afforded substances of intermediate oxidation such as carboxylic acids. Prior to 1900, chemists had reacted O_3 with many crude organic substances such as straw, humus, blood, *etc.*, and had reported some isolated reactions of pure substances, including the conversion of indigo to isatin, of benzene and other aromatic compounds to explosive solids, and of ether to a peroxidic substance without any rational examination of the chemistry involved. The only work of any systematic nature which appeared before 1900 was a single long paper by *Otto* [4] in 1898 in which he reported oxidations of a variety of organic compounds (hydrocarbons, amines, phenols, *etc.*) and showed that a number of aromatic compounds with unsaturated side chains were converted to aromatic aldehydes including the synthesis of vanillin from isoeugenol (see below).

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[1]) For Parts I and II, see [1].

The utility and importance of O_3 in organic chemistry was established largely by the systematic efforts of *C. D. Harries* during the period 1903–1916. His interest in O_3 arose from an interest in the structure of rubber. Based on very early observations [5] that rubber tubing was attacked by O_3, he considered that ozonolysis might be a useful method for studying the structure of rubber, provided that there was sufficient knowledge of the reactions of ozone with simple compounds. Beginning in 1903 in Berlin and continuing in Kiel, he published *ca.* 80 papers on the subject, including four long summary articles in *Liebigs Ann. Chem.* in 1905 [6], 1910 [7], 1912 [8], and 1915 [9], which included his views on the status of ozone chemistry as well as reports of original work. A volume of collected papers [10a] published in 1916 included reprints of all of *Harries*'s own work as well as the habilitation lectures of a number of his younger colleagues.

The 1905 summary [6] included a drawing of the ozonolysis laboratory. It showed a motor generator to produce 110-V alternating current from the direct current available at that time, a transformer to convert this to *ca.* 10,000 V AC, and cylinder oxygen with a drying train. The dried O_2 supply was connected to an all-glass apparatus incorporating ten *Berthelot* tubes for generating O_3 from O_2 (used either in series or in parallel; use in series gave somewhat higher O_3 concentrations [7]) with Hg seals. The O_3/O_2 mixture was bubbled through a cooled reaction vessel containing the solution of substance being investigated, This reaction vessel also included CO_2 inlet and outlet tubes to replace the oxidizing atmosphere. The correct iodimetric procedure [1b] was generally used for analysis of O_3 concentrations. The apparatus produced *ca.* 5% O_3 in O_2 in 1905; this increased later [11] to 10% and then to *ca.* 15%. Reaction times were in the order of 1 h or less per gram of organic compound. Cooling of the reaction solutions was usually achieved by the use of salt/ice mixtures; a dry ice/ether bath (*ca.* $-70°$) was used with ethylene in MeCl solvent and with propylene in EtCl solvent. Reaction progress was monitored by testing aliquots with bromine until complete consumption of alkene was indicated by the fact that the solution no longer decolorized bromine.

In some cases, reactions were run in aqueous or AcOH solutions, and the final products were isolated directly, sometimes after heating. However, recognizing [6] [12] from his own work [13], as well as earlier work of *Berthelot* [14][2]) and others, that the initial product of reaction of O_3 with most organic compounds was a highly reactive peroxidic material, much of the work was performed in carefully dried, low-boiling solvents [15], which could be evaporated to yield the crude initial product(s) resulting from addition of O_3 to the organic substrate. This most important point, namely that ozonolysis of alkenes involved two steps, first addition of O_3 to alkene and then reaction of the initial product in a subsequent step, had been ignored completely by earlier workers with ozone; it was clear to *Harries* almost from the beginning of his work and represented an important breakthrough in the study of O_3 reactions. The initial peroxidic products were named ozonides[3]) by *Harries* to distinguish them from

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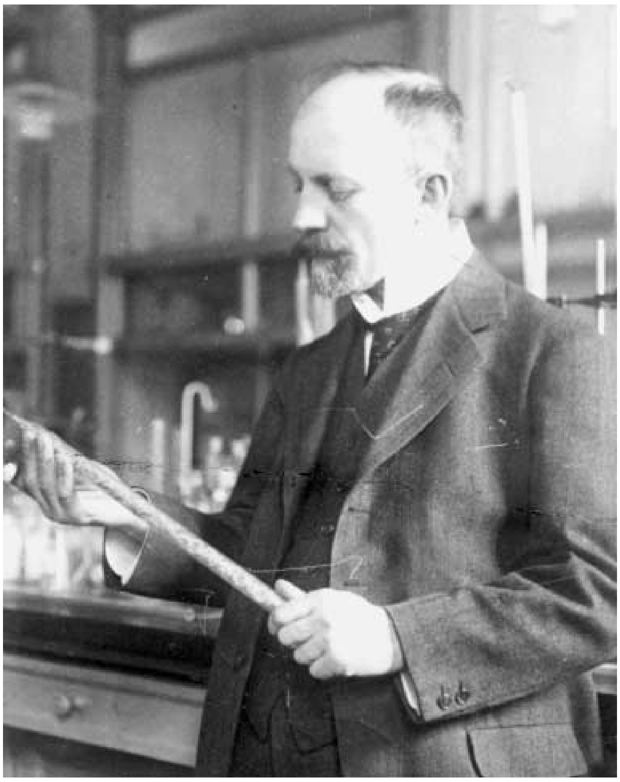
[2]) *Harries* [15] attempted to repeat the work of *Berthelot* but found the product of ozonolysis of diethyl ether to be too explosive for safety.

[3]) *Schönbein* had used this term for the higher oxides of inorganic compounds, such as silver peroxide formed by ozonolysis, that reverted to normal oxides on heating. However, it had not come into general use, and *Harries* gave it a new meaning that has persisted to the present time.



Carl Dietrich Harries, 1866–1923. (Photo courtesy of the *Siemens Archives*, Munich)

Carl Dietrich Harries was born in Luckenwalde, Germany, to a family of jurists. After brief periods at Jena and Munich, he continued his university studies in Berlin where he received his doctorate in 1892 under *Tiemann*. *Harries* then became an assistant to *A. W. Hofmann* in Berlin and, after *Hofmann*'s untimely death that same year, assistant to his successor, *Emil Fischer*. He rose through all the academic ranks from lecture demonstrator to associate professor. In 1900, he married *Hertha von Siemens*, daughter of the electrical genius *Werner von Siemens*, co-founder of the *Siemens* and *Halske* company (now *Siemens AG*) and the inventor of one of the earliest (and best) ozone generators. With the help of *Siemens* and *Halske*, *Harries* started a research program on ozonolysis. In 1904, he moved as full professor to the University of Kiel, where he remained until 1916. Dissatisfied with many of the petty aspects of academic life in Kiel and having failed to obtain either of two coveted positions at more prestigious universities, he left academia to become Director of Research at *Siemens* and *Halske* in 1916. Three years later, he declined the offer of a chair at the University of Göttingen. He died on November 3, 1923, of complications following surgery for cancer. A lengthy appreciation of the life and work of *Harries* has been written by *Willstätter* [10b].

other types of peroxides. They were thermally sensitive compounds, sometimes highly explosive, that could be purified, in lower-molecular-weight cases, by cautious distillation at reduced pressure. Occasionally, crystalline ozonides were encountered. Otherwise, the solvent was removed by prolonged evacuation, and the residue was investigated without any purification. Combustion analyses and cryoscopic molecular-weight determinations could be performed with suitable care; these showed that the ozonides were addition products ($R \rightarrow RO_3$; see below) of O_3 to double bonds. Dimeric ozonides were also observed. Ozonides decolorized indigo and permanganate solutions and liberated I_2 from KI but reacted only slowly with Br_2 in AcOH. The latter observation provided a method to monitor progress of reaction, as mentioned above. Subsequent reaction of ozonides with H_2O or AcOH afforded the stable products of reaction: aldehydes and/or ketones and/or carboxylic acids resulting from cleavage of double (or triple) bond(s).

When he left the University of Kiel in 1916 to become Director of Research at *Siemens* and *Halske*, *Harries* had established:

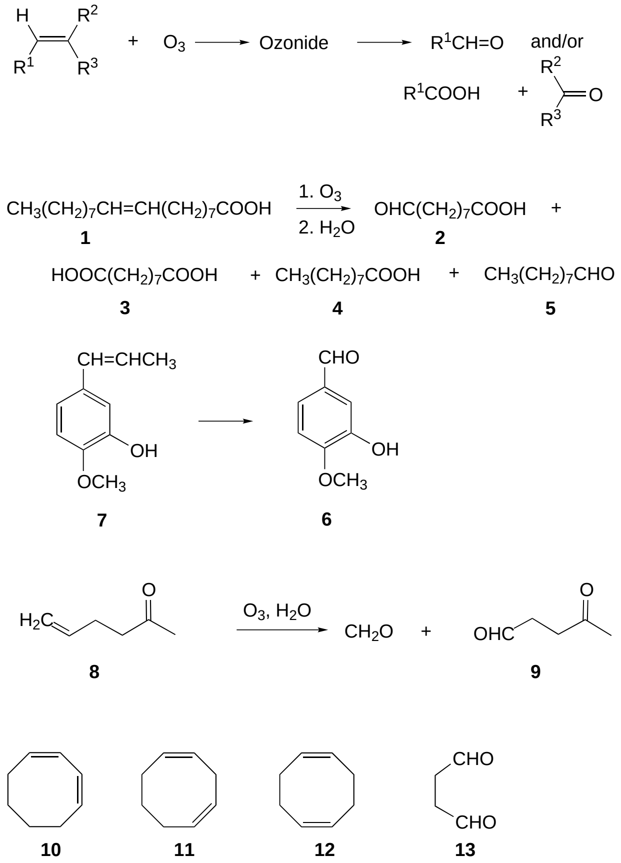
1) the course of reaction of O_3 with a large variety of organic compounds, *2*) the value of ozone in organic synthesis, *3*) the great utility of O_3 for determination of the structures of organic compounds, and *4*) he had made valiant attempts to understand the mechanism of reaction.

2. Reaction of O_3 with Organic Compounds (*Scheme 1*). – *Harries* investigated [6–9] the reactions of O_3 with a wide range of olefins. These included simple olefins such as ethylene, propylene, butenes, amylenes, five-, six-, and seven-membered cyloalkenes, a variety of alicyclic and cyclic terpenes, *etc.*, as well as dienes that underwent addition of two molecules of O_3, trienes (benzene gave a triozonide [17]), naphthalene, *etc.* Olefins with a variety of additional functionalities including carboxylic acids, ketones, alcohols, amines (as their ammonium salts [18]), halogens, *etc.* were also investigated. A conclusion drawn from this work was that an addition reaction occurs between any type of double bond and O_3 to give the 1:1 addition products, the ozonides. Subsequent workup (H_2O, AcOH, *etc.*, see below) of ozonides produced aldehydes and/or ketones, and/or carboxylic acids. Whenever either terminus of the double bond included a H-atom, the final product from that terminus could be either an aldehyde or a carboxylic acid or both; ketones were obtained whenever the terminus was disubstituted. In a few cases, ketone peroxides were obtained. The possibility of rearrangement [19] occurring during the reaction was excluded. Supposed examples of rearrangement, such as in the ozonolysis of citronellol, were shown to have been due to the fact that the material used was a mixture of citronellol with the double bond isomer rhodinal. *Harries*'s conclusion, valid to the present day, was that the oxidative cleavage of alkenes by O_3 is a straightforward general reaction of wide utility.

Triple bonds were also cleaved by O_3 and gave carboxylic acids [20] in spite of *Molinari*'s claim [21] that acetylenes did not react. *Harries* failed to observe the intermediate formation of α-dicarbonyl compounds in the reaction with alkynes. This was demonstrated in 1920 by *Wohl* and *Bräunig* [22], who showed that acetylene itself was converted into glyoxal.

While many workers exploited *Harries*'s discoveries, most new explorations of O_3 chemistry were performed in his laboratory. His priority in the field was generally

Scheme 1



recognized4) except by the Italian chemist *Molinari*5) [21], who claimed priority in the field for himself despite *Harries*'s strenuous objections, and who also reported a number of erroneous results such as his conclusion that triple bonds and aromatic compounds do not react with ozone. At one point *Harries* was led to comment [23]: *'This is the third time that I have had to take the trouble to check and correct* Molinari*'s major mistakes.'*6). He later refused to engage in further polemics with

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4) It was generally accepted at that time that a research group might claim a specific area of chemistry as its own, and that others would then avoid working in this area, in an interesting contrast to present times.

5) *Ettore Molinari*, 1867–1926. Studied in Zürich and Basel; Dr. Phil. 1889 Basel. He then traveled for a year in Germany, France, and England, and spent a year in Heidelberg followed by several years in the Italian chemical industry. In 1900, he moved to the new trade school in Milan and eventually became Prof. chim.-tecnol. and Dir. Ist. chim.-tecnol., R. scu. d'Ingegneria, Milano. His handbooks and textbooks of applied chemistry were translated from Italian into English, French, and Spanish.

6) '*Es ist nun schon das dritte Mal, dass ich mir die Mühe geben musste, Hrn.* Ettore Molinaris *kapitale Irrtümer nachzuprüfen und richtigzustellen.*'; rough English translation by the author. Shortly afterwards, *Molinari* retired from ozone chemistry.

Molinari, leaving the rights and wrongs to be decided by time and the judgment of colleagues.

Oximes were shown to undergo an analogous cleavage [24], which *Harries* suggested might also involve an intermediate ozonide.

Harries distinguished [7] between the reactions of alkenes, where the entire molecule of O_3 is incorporated into the initial reaction product, and those where the molecule of O_3 undergoes cleavage with one O-atom appearing in the reaction product and the remaining two atoms appearing as molecular O_2. The latter reaction is typical of saturated hydrocarbons (which form alcohols and higher oxidation products), alcohols (form aldehydes) [25], and aldehydes (form carboxylic acids). These were relatively slow reactions, except for aldehyde oxidations [26] where the rapidly formed labile peroxides were converted to carboxylic acids in the usual workup procedures.

3. Applications of Ozone in Organic Synthesis. – *Harries* exploited the ozonolysis reaction for the synthesis of a variety of difficultly obtainable substances including levulinaldehyde [13], glyoxal and its monoacetal [27], methylgyloxal [28], mesoxaldehyde [27], biacetyl carboxylic acid [29], and succinic acid semi-aldehyde [30], among others. While these were significant achievements, the work was severely hampered by the finding that the usual procedure for decomposition of ozonides, heating with H_2O, afforded H_2O_2 as well as ketones, and both aldehydes and acids in compounds having a H-atom at either terminus of the double bond. For example, ozonolysis of oleic acid (**1**) [30] afforded azelaic acid semi-aldehyde (**2**), azelaic acid (**3**), nonylic acid (**4**) and nonylic aldehyde (**5**); four products rather than the desired two. This result complicated the isolation procedures and reduced the yields of individual products. In the later part of his work, *Harries* introduced the use of Zn and AcOH for workup of ozonides, which afforded only aldehydes and/or ketones; *e.g.*, only nonylic aldehyde and azelaic acid semi-aldehyde were formed from oleic acid.

This improved procedure, the use of Zn in AcOH, was first introduced as part of a re-investigation of the synthesis of vanillin (**6**) from isoeugenol (**7**) originally reported by *Otto* [4]. A French company had taken out a patent and produced appreciable quantities of vanillin by this procedure[7]. Their application for a German patent was refused after their procedure was checked by Witt[8]) who obtained only a 3% yield of vanillin following the French procedure. The disturbing implication that *Harries* (and others) drew was that nationalistic considerations had intruded into the German patent office. Eventually, the question was re-examined by *Harries* [33], who argued that *Witt* had used much higher concentrations of O_3 than the French workers, resulting in overoxidation of the initially formed vanillin, which contains both a reactive aldehyde

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[7]) *Bridge* [32] stated that the vanillin plant operated by the *Société Française de l'Industrie Chimique 'produced 22 metric tons of vanillin in a single month in 1903'.* This plant was closed some time later, presumably because of unprofitability.

[8]) *Otto Nikolaus Witt*, 1853–1915, born in St. Petersburg, where his father was professor in the apothecary school. He received his first degree from the ETH, Zürich, and had a distinguished career in the dye industry followed by an academic career in Berlin. In 1876, he clarified the structures of azo dyes. *Witt* habilitated at the Technische Hochschule in Charlottenburg, Berlin, where he became full professor of Technical Chemistry in 1891. He used absorption spectra in his work and emphasized the relationship between color and constitution. *Witt* coined the terms chromophore and auxochrome.

group and an activated aromatic ring. The ozone generators used in the early French work produced low concentrations of ozone, whereas *Witt* used a more-efficient *Siemens and Halske* ozone generator. *Witt* [34] stood angrily by his guns, claiming that his results were entirely objective, and that he had used various O_3 concentrations in checking the French patent application. Be that as it may, a 71% yield of vanillin was obtained in the *Harries* laboratory by reducing the O_3 concentration to *ca.* 3% and by using Zn in AcOH acid for workup of the ozonide. Meanwhile, the French company had gone out of business, and the truth of the whole affair remains unclear.

Synthetic applications of the ozonolysis reaction continue to the present day using a variety of workup procedures unknown in *Harries*'s time.

4. Structure Elucidation (*Scheme 1*). In his very first ozone paper [13], *Harries* proposed that O_3 could be used to establish structures of alkenes. The argument was very simple. Since O_3 cleaves a double bond to produce two fragments, each containing a carbonyl group at the original location of the double bond, it is only necessary to identify the products of reaction in order to establish the termini of the double bond. The two pieces can then be jointed to give the original alkene structure. His first example was the structure of allyl acetone (**8**), which produced levulinaldehdye (**9**) plus formaldehyde (and/or formic acid) on ozonolysis. Another simple example concerned a cyclooctadiene that *Willstätter* and co-workers had obtained in their work on pseudopelletierine. Three cyclooctadiene structures, **10**, **11**, and **12** could be considered. By arrangement with *Willstätter*, *Harries* [35] received a sample of this material and found that ozonolysis produced only succindialdehdye (**13)** and succinic acid. The compound, therefore, had to be the cycloocta-1,5-diene (**12)**.

The number of double bonds in a molecule could also be determined from the oxygen content of the corresponding ozonide, providing a complement [9] to such determinations by catalytic hydrogenation. Ozonolysis was also useful in determining whether two isomeric alkenes were *cis*–*trans* isomers. If they were, both substances would give identical products of ozonolysis, otherwise the products would be different. For example, **1** and elaidic acid were shown [36] to be *cis*–*trans* isomers by this procedure and *Wislicenus*'s crotonic and isocrotonic acids were similarly proved [37] (see also [10])to be *cis-trans* isomers, as *Wislicenus* had suggested.

Ozonolysis was quickly adopted by chemists investigating the structures of organic compounds, particularly natural products. For example, by 1919, more than 60 publications had appeared in which ozonolysis had been applied to structure problems, including such (then) esoteric subjects as the structures of enols [38]. *Semmler* alone [39] had reported the use of O_3 in at least 18 papers on his investigations of terpene structures.

Application of the sequence, exhaustive methylation of amines, *Hofmann* elimination from the resulting quarternary salts to give alkenes, and, finally, ozonolysis, was of major importance in the structure determination of a host of alkaloids. As noted in the *Introduction*, the contribution of ozonolysis to the study of compounds of unknown structure was invaluable until the development of sophisticated spectroscopic techniques in the latter part of the 20th century.

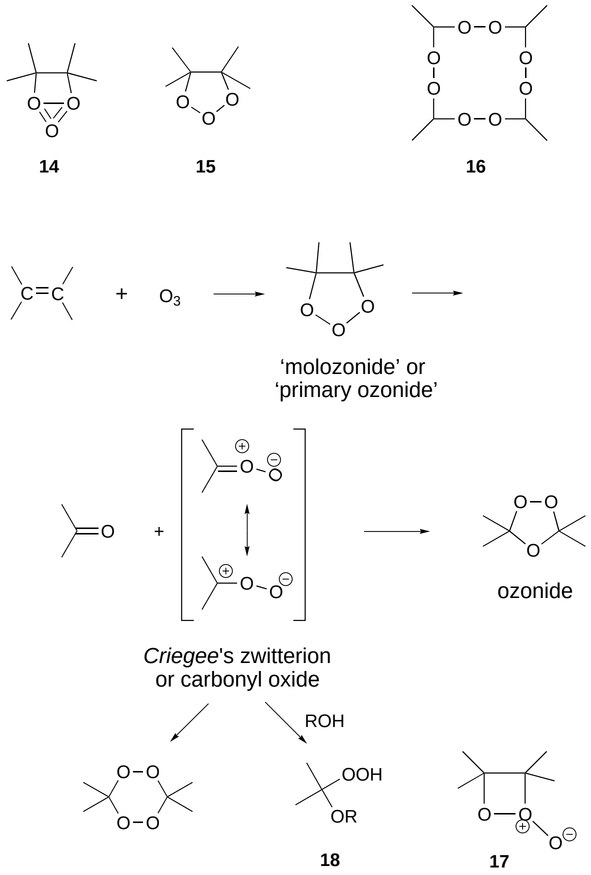
In a number of papers, *Harries* reported experiments with complex natural products; the results were of limited value. These included work on rubber [40], casein [41], and brown coal [42].

5. Mechanistic Investigations (*Scheme 2*). – *Harries* also attempted to clarify various mechanistic aspects of ozonolysis. Considering the tools available to the organic chemists of his time, it is not surprising that he made limited progress, and that much of his work in the mechanistic area had to be clarified by later workers. He originally formulated [6] the ozonide as a bicyclic addition product **14** of O_3 to a double bond but later [7] represented it by the monocyclic structure **15** (the present primary or molozonide); in both cases, the original C-skeleton of the substrate *remained intact*. Structure **15** was preferred over **14** on the basis of molecular-refraction measurements.

The survival of the intact original C-skeleton relied on the observation that the ozonide obtained (without purification) from mesityl oxide [43] afforded a low yield of starting mesityl oxide upon treatment with H_2O, in addition to the expected cleavage products. This result could not be repeated. It was later attributed by *Pummerer* and *Richtzenhain* [44] to incomplete reaction of (relatively unreactive) mesityl oxide; the observed result was due to the presence of unreacted starting material in the crude ozonide and not to reversion of ozonide to starting material. A report by *Harries*, lacking any experimental detail, to the effect that fumaric acid behaved like mesityl oxide could also not be confirmed; fumaric acid reacted extremely slowly with ozone. Attempts to reduce ozonides to vicinal glycols, an expected result if the structure **15** is correct, were not successful. The techniques of *Harries*'s times were not adequate for the difficulty of the problem. Well over half a century elapsed before it could be shown by very low temperature NMR methods that **15** was, in fact, the structure of the initial product of addition of ozone to a double bond *via* 1,3-dipolar cycloaddition.

Additional confusion was created by *Harries*'s report [45] that products incorporating four O-atoms per double bond were formed in some alkene reactions. With unsaturated carbonyl compounds, this was attributed to addition of an O-atom to the carbonyl O-atom; the resulting 'carbonyl peroxides' reverted to the initial carbonyl group upon treatment with H_2O. However, a variety of other alkenes were also reported to give products containing four O-atoms; *Harries* called these 'oxozonides'. He suggested the existence of an allotrope of oxygen having the molecular formula O_4 ('oxozone') that added to multiple bonds analogously to O_3 to give the oxozonides. Oxozone supposedly was removed by passing the initially formed product from silent discharge (*Berthelot*) tubes through aqueous sodium hydroxide solution, followed by concentrated sulfuric acid for drying. The resulting decrease in the titer for active oxygen (on the order of 25% or more) supposedly reflected the destruction of O_4; ozone treated in this way gave normal (O_3) ozonides. Oxozone disappeared almost immediately from the chemical literature, but, within only a few years, *Lewis* [46] suggested the existence of a metastable dimer of oxygen, the species O_4, having nothing to do with the oxidation of organic compounds. This and other allotropes of oxygen have been of interest for many years. About 25 years after *Harries*'s work, *Rieche et al.* [47] proposed that the dimeric 'oxozonide' from ozonolysis of but-2-enes had the peroxide structure **16**, corresponding in molecular composition to $(C_4H_8O_4)_2$, but not an oxozonide at all. It also appears possible that the high analytical values for oxygen that led to the proposal of oxozone may have been the result of overoxidation (*e.g.*, of C−H bonds) at high concentrations of ozone. It should also be noted that *Harries*'s analyses were, perforce, often performed on crude ozonides that had undergone no purification except prolonged evacuation to remove reaction solvent.

Scheme 2



Some work was also done [7][48] on the rates of reaction of ozonides of cyclic alkenes in boiling water.

Any discussion of ozonolysis of organic compounds would be incomplete without at least brief mention of the brilliant work of *Rudolf Criegee*⁹) [49]. He applied almost all of the experimental tools available to the physical organic chemist in the middle of the 20th century to weave together the ideas of *Harries*, *Staudinger*, *Pummerer*, *Rieche*, and others into a unified reaction mechanism (*Scheme 2*), which has required only some

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[9]) *Rudolf Criegee*, 1902–1975; born in Düsseldorf to a family of jurists. *Criegee* studied in Tübingen and Greifswald before completing his doctorate in Marburg under the direction of *Otto Dimroth* in 1925. He habilitated in 1930 and, in 1932, moved to his first university position at Marburg. *Criegee* became associate professor in Karlsruhe in 1937, full professor in 1947, and remained in Karlsruhe for the rest of his career, although he did not lack for calls to other universities. In addition to his seminal work with O_3, he made important contributions to a variety of other oxidation reactions, including lead tetraacetate and singlet oxygen, as well as to the chemistry of small ring compounds.

fine tuning during the nearly 50 years since it was first proposed. The *Criegee* mechanism[10]) for formation of the ozonide involves three 1,3-dipolar cycloaddition processes: the first one produces the primary ozonide (identical to *Harries's* ozonide formulation), the second is a 1,3-dipolar cycloreversal to give a carbonyl compound plus *Criegee*'s zwitterionic intermediate (often called a carbonyl oxide), and, finally, a third 1,3-dipolar cycloaddition to give the isolable ozonide. *Criegee* could not distinguish between the primary ozonide structure shown and the *Staudinger* proposal, **17**, although one may conclude that he preferred the former. The variety of other products (simple and polymeric) that may be observed in special cases are all accounted for by this scheme. For example, *Rieche*'s peroxide, **16**, is the tetramer of a *Criegee* zwitterion and the alkoxy hydroperoxides **18** obtained from ozonolyses in alcohol solution are simply the addition products of a molecule of alcohol to the zwitterion.

6. Conclusions. – In conclusion, it is clear that the introduction of O_3 into organic chemistry was due in large part to the work done in the laboratory of *C. D. Harries* during the period 1903–1916. Much of his theoretical work suffered from his fertile imagination and the limitations of the period during which he worked and is of little value today. However, the large body of experimental work and the conclusions regarding the chemical reactions of organic compounds with O_3 are as relevant today as they were nearly one hundred years ago. Thanks to *Harries* and his co-workers, O_3 has contributed enormously to the progress of organic chemistry.

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