groups capable of forming useful films by combining with components contained in a second package. The distinguishing feature between the two types of two-package systems is that in one the second package contains a relatively *small* amount of a catalyst, accelerator or crosslinking agent such as a monomeric polyol or polyamine and in the other the second package contains a *substantial* amount of a resin such as blown castor oil which has reactive hydrogen groups. The systems have a limited pot life after the two packages are mixed.

The major applications of polyurethanes are in foams, elastomers and coatings. Derivatives of fats and oils have a place in all of these—provided adequate research is done to find and keep it.

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Reactions of Ozone. VII.

Ozonization of Fatty Acids and Their Derivatives

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Abstract

Ozone was a useful tool very early in the history of structural studies involving fatty acids and their derivatives. More recently the productions of azelaic and pelargonic acids by the ozonolysis of oleic acid has become of commercial importance. This paper reviews the chemistry of the ozonolysis of various unsaturated fatty acids and their derivatives. The products can be varied from a single starting material depending on the manner of decomposing the intermediate ozonide. Thus, variations in starting material and variations in procedure make possible a great variety of straight chain products containing one or two functional groups such as carboxyl, aldehyde, hydroxyl, and amino.

Introduction

In the decade 1951–61, ozonization chemistry has mushroomed in its use as a general chemical tool of the synthetic chemist working with unsaturated fatty acids, oils and their derivatives. This is evidenced by the accelerated growth of *primary* ozone publications explaining some new facet of organic ozone chemistry as shown in Figure 1.

In addition, numerous papers describing the use of ozone as a step in a reaction sequence have been published. No special mention of ozone was made there because of the increasing acceptance of ozone for everyday use by laboratories that have ozonators on hand. There are 450 to 475 laboratory ozonators in the U.S. to date.

The versatility and useful applications of ozone for unsaturation values, structure determinations, production of mono and polybasic acids, aldehydes, amines, omega-amino acids, amine oxides, peracids and epoxides are coming into their own as discussed below.

Discussion

Unsaturation

For years a simple, reliable, quantitative method for determining olefinic unsaturation has been sought. Existing methods such as bromination, iodination, catalytic hydrogenation and peroxide reactions have their specific limitations as discussed by numerous investigators (2,5,23,31). However, for many olefinic compounds, ozone is an excellent titrimetric reagent (23). Maggiolo (19), Boer and Kooyman (6) have shown that ozonization could well supplant these other methods. The procedure can be simplified by using commercially available apparatus. The analysis is based on determining the time required to titrate a sample of olefin with a stream of ozonized air containing a known amount of ozone.

This proposed analytical determination eliminates most of the limitations and failings found in the current bromine and iodine number procedures. The presence of tertiary hydrogens as in α-pinene does not cause the high varying results found by the bromine technique. The determination of olefinic unsaturation in the presence of an activated aromatic ring as in isosafrole is also shown to be feasible. The results given in Table I are expressed as "Ozone Values," i.e., the number of grams of ozone absorbed per 100 g of unsaturated fatty acid.

Samples containing small amounts of conjugated

TABLE I

Compound	Ozone value theory	Ozone value found
Methyl oleate	16.2	16.2, 16.4
Linoleic acid	34.2	34.2, 34.4, 34.4, 34.5
Methyl linolenate	49.2	49.2, 49.5
Isosafrole	29.5	29.0, 29.7, 29.1
α-Pinene	35.3	36.1, 35.6
Olive oil	16.4	16.3, 16.5
Sesame oil	21.3	21.7, 21.7
Safflower oil	27.1	27.5, 27.5, 27.8
Tall oil	24.3	24.3, 24.5
Tall oil	23.9	23.8

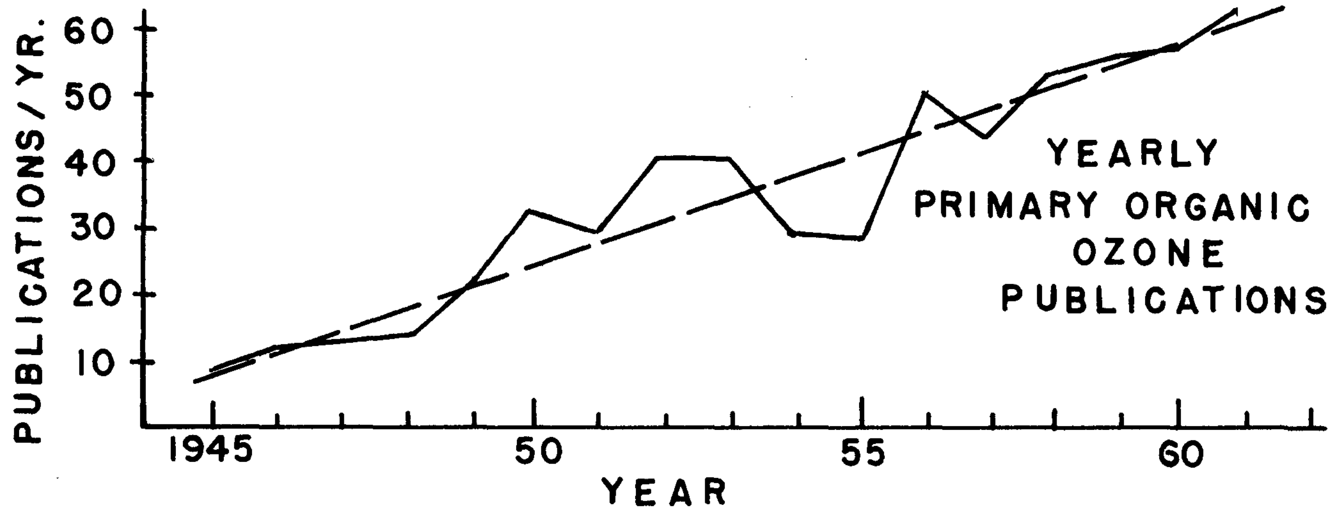


FIG. 1.

unsaturation such as tall-oil fatty acids can be satisfactorily determined. However, if a substantial portion of the unsaturation is slow reacting, as in the remaining double bond of a conjugated system such as 2,5-dimethyl-2,4 hexadiene or in sterically hindered compounds (6), a slight loss of ozone into the KI solution occurs. With these slow reacting compounds the endpoint is obscured and the standard procedure is not applicable. In these cases, ozone concentration can be determined using an ozone meter. Plotting ozone concentration versus time gives an endpoint as a sharp break in the curve. The integration of the area under the curve gives the total absorbed ozone. The results are shown in Table II.

Structure Determinations

Ozone is an extremely valuable tool in structure determinations, especially in proving where a particular double bond is located. If the compounds are polyunsaturated, the speed of ozone attack, lack of side reactions, including inability of shifting double bonds, has been universally recognized.

The ozonolysis products from unsaturated fatty acids have been identified by oxidation to acids and analysis by chromatography (17,18). Fies, Holasek, and Lieb (13) used ozone for the detection of unsaturated fatty acids. Unsaturated fatty acids from a mixture of fatty acids separated by paper chromatography are made visible by treatment of the chromatograph with ozone followed by spraying with fuchsin-H_2SO_3.

An improved procedure for the determination of structure by reductive ozonolysis was recently reported by Privett and Nickell (27). The ozonization was performed at about −60C by the addition of the unsaturated fatty acid as the methyl ester dissolved in pentane to a pentane solution of ozone. The ozonides are cleaved by reduction with a Lindler catalyst at 0C in pentane or other suitable solvent. The carbonyl compounds thus formed are analyzed by gas-liquid chromatography.

TABLE II

Compound	Unsaturation theory	Equivalent found	% Unsat. of theory
2,5-Dimethyl-2,4-hexadiene	55.1	57.3, 57.6	96.0
Cyclooctadiene 1,5	50.1–48.5	52.5, 54.4	95.
Maleic acid	115	119	97.2
Crotonic acid	86.1	86.2	99.8
Sorbic acid	56.1	57.4	97.5
Oleic-linoleic acids	199	202, 196	100.
Oleic-linoleic acids	201	203, 200, 203	99.6

Anders (3) in studying new reaction techniques of ozonization of unsaturated fatty acids at the 9, or 11 or 13 carbon atoms of unsaturation in methanol and pyridine obtained omega-formyl esters in 90% yield.

Oxidative ozonolysis of prostaglandin E methyl ester acetate yielded suberic, succinic and alpha hydroxyheptanoic acids reported by Bergstrom, Rthage, Samuelsson and Sjoval (4) enabled them to determine its structure.

The chemistry of pinolic acid and its acid catalyzed rearrangement was solved by Hedrick et al. (24). One of the key steps was the selective ozonization of 2,2,4-trimethyl-3-cyclopentene-1-acetic acid to give isocamphoronic acid.

Products from Ozonization of Double Bonds

Aldehydes. The effect of solvent and pH on the ozonization of methyl oleate and subsequent reductive decomposition is reported by Pryde et al. (28) who obtained crude yields of 90–95% of pelargonyl aldehyde and the half aldehyde of azelaic acid. The use of reactive (participating) solvents such as methanol in the ozonization step, coupled with the use of pyridine to render the solution slightly basic, increased aldehyde yields by inhibiting secondary rearrangement and preventing acetal formation.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \xrightarrow[CH_3OH]{O_3}$$

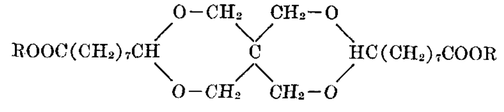
$$\longrightarrow \left\{ \begin{array}{l} CH_3(CH_2)_7-CHO \\ \quad \text{or} \\ CH_3(CH_2)_7-CHOOH-OCH_3 \\ \quad + \\ CH_3OOC(CH_2)_7-CHO \\ \quad \text{or} \\ CH_3OOC(CH_2)_7-CHOOH-OCH_3 \end{array} \right.$$

The same group extended this study to the preparation of C-11, C-12, and C-13 aldehyde esters. The C-11 and C-13 aldehyde esters were prepared from methyl 11-eicosenoate and methyl erucate, respectively. These two monoenoic esters were isolated by fractional distillation of crude methyl erucate on a spinning band column. The C-12 unsaturated aldehyde ester was prepared by partial ozonization of methyl linoleate.

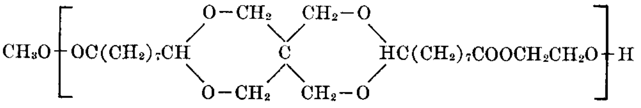
Saturated and partially unsaturated aldehyde glyceride oils were also prepared by ozonization of soybean oil. These aldehyde oils are viscous, colored liquids having 2.4 to 2.6 aldehyde groups per glyceride molecule. They are highly reactive toward urea, polyols, and phenolic compounds. The products from these various reactions are soft, flexible, but infusible and insoluble gels, indicating a high degree of crosslinking.

The partial ozonation gave products with lesser degree of aldehyde functionality but having some residual unsaturation which is available for further reactions. Such products, containing three different types of functionality-aldehydic, olefinic and the glyceride ester groups, should be useful modifying agents for many plastic applications.

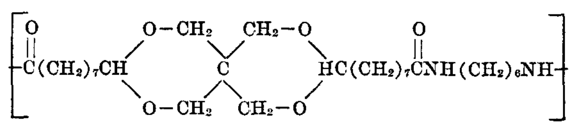
Poly(ester-acetals) and poly(amide-acetals) and methods of crosslinking them show a great deal of promise in glass and metal adhesive applications. A series of these were made from the methyl half-aldehyde ester, methyl azelaaldehydate, obtained in 85–90% yield from ozonolysis of methyl oleate (28a,28b).



Di-methyl Azelaaldehydate-Pentaerythritol Acetal

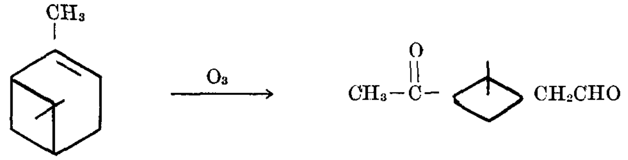


Homopoly (Ester-Acetal) of Ethylene Glycol

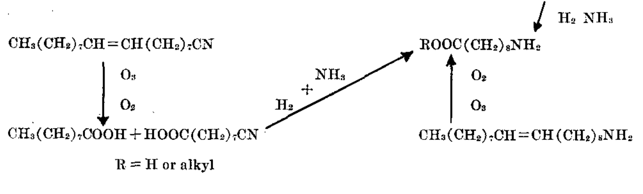


Homopoly (Amide-Acetals) of Hexamethylene Diamine

Eschinazi (10) has developed a commercial process for the preparation of pinonic aldehyde by ozonolysis of α-pinene in the presence of a water-miscible solvent and then warming with a reducing agent.



Aminopelargonic acid is made by reduction of azelaaldehydic acid with ammonia and hydrogen or by reduction of its oxime. The amino-acid is polymerized to yield the nine-carbon nylon called Azelon. Azelon (nylon-9) is produced in Japan in limited quantities. It is also made from oleyl nitrile or oleyl amine.



R = H or alkyl

Some very recent process improvements on reductive methods have been reported by Diaper and Mitchell (8). By reductive amination of the ozonolysis products of the terminal olefins 10-undecen-1-ol, ethyl 10-undecenoate and 10-undecenoic acid they produced 10-amino-decan-1-ol, ethyl 10-aminodecanoate, and 10-aminodecanoic acid, respectively. Esters are also formed in a competitive reaction, by thermal decomposition of the ozonolysis products.

$$HO-CH_2(CH_2)_8CH=CH_2 \xrightarrow{O_3} \xrightarrow[C_2H_5OH]{H_2+NH_3} HO-CH_2(CH_2)_8CH_2NH_2$$

$$C_2H_5OOC(CH_2)_8CH=CH_2 \xrightarrow{O_3} \xrightarrow[C_2H_5OH]{H_2+NH_3} C_2H_5OCO(CH_2)_8CH_2NH_2$$

$$HOOCCH_2(CH_2)_8CH=CH_2 \xrightarrow{O_3} \xrightarrow[C_2H_5OH]{H_2+NH_3} HOOCCH_2(CH_2)_8CH_2NH_2$$

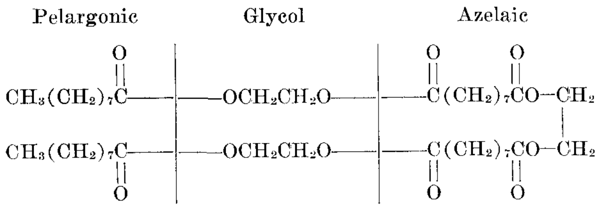
Alcohols. Diaper and Mitchell (9) have also reported an improved preparation of ω-hydroxy aliphatic acids and their esters. Reductive cleavage of the ozonides of aliphatic acids and their esters by sodium borohydride or by hydrogenation produces ω-hydroxy aliphatic acids and their esters, respectively, in high yields.

Pfeiffer, Brandon, and Swidler (26), in their patent for the preparation of hydroxy pelargonic acid and its derivatives claim "a process for the manufacture of a hydroxy compound selected from a group consisting of ω-hydroxy pelargonic acid and lower aliphatic alcohol esters comprising: catalytically hydrogenating an ozonide selected from the group consisting of ozonides of oleic acid and ozonides of lower aliphatic alcoholic esters of oleic acid in the presence of free hydrogen and Raney nickel at a pressure in the the range of 200–3000 lb/sq in., heating the materials so hydrogenated to a temperature in the range of 60C to 150C and recovering said hydroxy compound from the reaction mixture in yields greater than 60% of theory and substantially free of aldehydic by-products."

Monobasic and Dibasic Acids. Ozonolysis of oleic acid and unsaturated tall oil fatty acids which are readily available today at 6 to 10¢/lb in tonnage quantities represent a very economical source of caproic, pelargonic and azelaic acids. This type of process is described in patents by Goebel (14) and Maggiolo (20) as well as excellent but more elaborate procedures by Ackman (1) and Pasero (25).

Low Molecular Weight Polymeric Plasticizers. Experiments on the ozonolysis-oxygen axidation of oleic or tall oil unsaturated fatty acids may offer an oxidate mixture having a fortuitous ratio of mono and dibasic acids that can be esterified by reacting with a glycol to form low molecular weight polymers [500 to 2000 M.W. Range (21)].

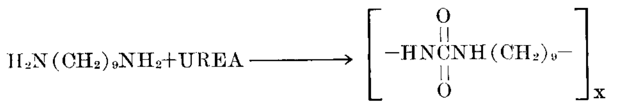
Polyester placticizers of low molecular weight that are derived from about 2 moles of monobasic acids (C_6 to C_{18}), 2–3 moles of a dibasic acid as an azelaic acid and about 3 moles of a glycol (ethylene, propylene or dipropylene glycol) and very useful general purpose plasticizers for polyvinyl chloride. They offer low volatility and outstanding migration resistance. Sprang and Webster (29) have described some of these polyesters.



Low Molecular Weight Linear Polymeric Plasticizers

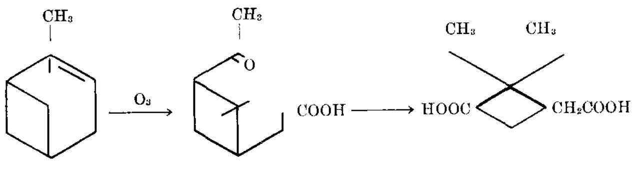
Polyureas. Urylon, which is now in semi-commercial production in Japan, has the usual good nylon properties with the added feature of low water adsorption and high tensile strength. It is made from azelaic acid, ammonia and urea.

$$HOOC(CH_2)_7COOH \longrightarrow H_2N(CH_2)_9NH_2$$



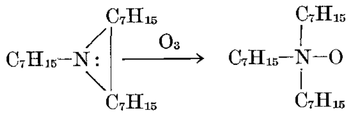
$$H_2N(CH_2)_9NH_2 + UREA \longrightarrow \left[-HN\overset{O}{\overset{\|}{C}}NH(CH_2)_9- \right]_x$$

Pinonic and Pinic Acid from a-Pinene. Hedrick and Lawrence (15) and Fisher and Stinson (12), U. S. Dept. of Agriculture, have in their investigations shown that pinonic acid and its derivatives can be made at a materials cost of 13¢/lb based upon it being made via ozonolysis of a-pinene, a major constituent of all American turpentines. This versatile compound has potentialities for polyesters, amino and dibasic acids, plasticizers, synthetic lubricants and merizing penetrants.

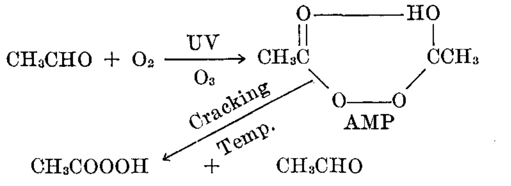


Oxidation Products

Tertiary Amine Oxides. It has been shown by Horner (16) and Maggiolo (22) that the formation of tertiary amine oxides by ozonization of tertiary amines is a general reaction for almost all kinds of tertiary amine. Several companies are currently test marketing amine oxides derived from fatty acids based on amine oxides as low sudsing detergents with bactericidal and antiseptic properties. A monograph entitled "Amine Oxides" has just been made available because of the growing commercial awareness of the antibacteria and surface active properties of certain fatty amine oxides.



Peracids and Epoxidations. Although Fischer, Dull and Volz (11) and Briner and Lardon (7) reported on the formation of peracids by the catalytic ozone-oxygen oxidation of aldehydes, which we had subsequently verified in our laboratory, a much improved practical break-through was achieved by Phillips, Frostick and Starcher (30). They perform an efficient two-step synthesis of a water-free solution of peracetic acid in an inert solvent. Acetaldehyde is autoxidized with oxygen and catalytic amounts of ozone at low temperature to an intermediate peroxide, acetaldehyde monoperacetate (AMP) which is then pyrolyzed to peracetic acid and acetaldehyde which are separated rapidly in a fractionating column.



Peracetic Acid Acetaldehyde

The peracetic acid is used directly in the production of many varied epoxy derivatives of unsaturated fatty acids as well as numerous olefins. The acetaldehyde is returned to process for the preparation of more peracetic acid. Acetic acid is a by-product which is used to make other products.

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