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A NEW AND CONVENIENT METHOD FOR CONVERTING OLEFINS TO ALDEHYDES

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The conversion of olefins to aldehydes by ozonolysis involves reduction of an ozonolysis product (1,2). Hitherto there has not been available a reagent which could be relied upon to effect this transformation in good yields. We now wish to report that dimethyl sulfide routinely effects such reductions under very mild conditions and in excellent yields (Table I); it should be emphasized that the yields reported in Table I relate to pure products actually isolated.

This new procedure hinges upon the fact that hydroperoxides are rapidly and cleanly reduced (3) to alcohols by sulfides, e.g. (4),

$$(CH_3)_3COOH + (CH_3)_2S \xrightarrow[CH_3OH]{25°} (CH_3)_3COH + (CH_3)_2SO \qquad (i)$$

TABLE I.

Conversion of Ozonized Olefins to Aldehydes

Using Dimethyl Sulfide

Olefin	Aldehyde	% Yield
Styrene	Benzaldehyde	89
Isosafrole	Piperonal	96
p-Nitrostyrene	p-Nitrobenzaldehyde	97
4-Vinylpyridine	4-Pyridinecarboxaldehyde	80
1-Octene	Heptanal	75
Phenanthrene	2,2'-Biphenyldicarboxaldehyde	91
Naphthalene	Phthalaldehyde	68[a]
	Glyoxal	66[a]
Maleic Acid	Glyoxylic Acid	91[b]
Diethyl Fumarate	Ethyl Glyoxylate Methanol Hemiacetal	73[c]
Diethyl Maleate	" "	71[c]
Cyclohexene	Adipaldehyde	62[d]

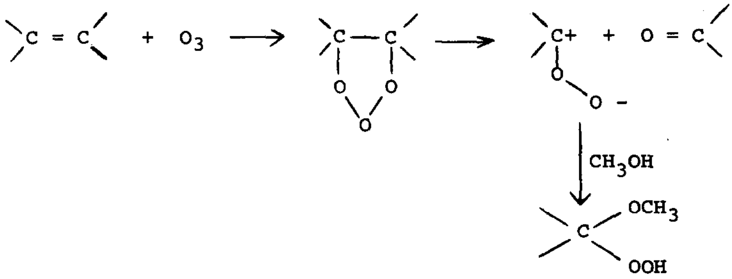
[a] As the bis[(2,4-dinitrophenyl)hydrazone].

[b] As the (2,4-dinitrophenyl)hydrazone.

[c] By direct distillation. Yields represent main fractions which are analytically pure. By vapor phase chromatography of all distilled fractions, yields are 87-92%.

[d] Direct distillation gives a 90% yield of a 1:1 mixture of adipaldehyde and dimethyl sulfoxide, b.p. 50-60° (2 mm.).

It is generally agreed (5) that ozonization of an olefin in a protic solvent such as methanol proceeds as follows:



(I)

It transpires that hydroperoxides of the type (I) react readily with dimethyl sulfide according to the pattern of eq. (i), i.e.,

$$\text{I} + (CH_3)_2S \xrightarrow[CH_3OH]{-10^\circ \text{ to } 25^\circ} {>}C=O + CH_3OH + (CH_3)_2SO \qquad \text{(ii)}$$

In addition to the rapidity with which it reduces hydroperoxides at low temperatures, dimethyl sulfide has a number of other virtues. It is highly selective, e.g., neither nitro groups nor carbonyl functions are reduced; the reduction is carried out under neutral conditions; any excess dimethyl sulfide is readily removed by evaporation (b.p. 37°) and the by-products, methanol and dimethyl sulfoxide, cause no purification problems (6).

As a typical example: A solution of 11.22 g. (0.10 mole) of 1-octene in 75 ml. of methanol is cooled to -30°. During the ozonolysis, the temperature is gradually lowered to -60°. Ozonized oxygen gas containing 65.2 mg. of ozone per liter of gas is passed through the solution at the rate of 1.0 l./min. until one molar equivalent of ozone has been absorbed. While still at -60° the system is flushed with nitrogen and 10 ml. (0.136 mole) of dimethyl sulfide is added. The solution is then stirred at -10° for one hour, then at ice bath temperature for one hour and, finally, at room temperature for one hour. The solvent is removed and the residue extracted with petroleum either (b.p. 30-60°) and water. The petroleum ether solution is washed with water, dried and evaporated. The residue, upon distillation, affords 8.58 g. (75%) of heptanal, b.p. 55-57° (20 mm.). The product is pure by infrared analysis and vapor phase chromatography. The aqueous layer is distilled to yield 6.14 g. (79%) of dimethyl sulfoxide, b.p. 46-51° (2 mm.).

This procedure is equal or superior to other methods (1,2,7,8). Of particular interest is the reduction of naphthalene ozonolysis products to phthalaldehyde. Bailey and co-workers (9) report that reduction of the methanolic ozonolysis mixture by sodium iodide in acetic acid gives rise to phthalaldehydic acid rather than to the dialdehyde and explain this on the basis that acid-catalyzed decomposition of the active oxygen intermediates occurs more readily than does reduction. Before arriving at the dimethyl sulfide reduction we applied the trimethyl phosphite technique of Knowles and Thompson (2) to the reduction of the methanolic ozonolysis mixture derived from naphthalene but, at best, obtained only a 26% yield of phthalaldehyde as the bis[(2,4-dinitrophenyl)hydrazone]. The dimethyl sulfide method, on the other hand, gives a 68% yield (Table I).

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4. Essentially quantitative yields of t-butanol and dimethyl sulfoxide were obtained by us.

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6. Still another useful attribute of this procedure is the fact that in some cases the reduced ozonolysis mixture can be distilled directly to give pure product when the boiling point of the product differs substantially from that of dimethyl sulfoxide (cf. Table I).
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