

Figure 1. Differential Thermal and Thermal Gravimetric Analyses of tetrazoleacetic acid, potassium salt.

Thermal Gravimetric Analysis. These data resembled data obtained from several other heterocyclic ring systems.³

However, during a routine drying operation involving a hot forced air tray dryer, kilogram quantities of the potassium salt of tetrazoleacetic acid violently exploded, resulting in damage to the dryer. Fortunately, no injury to personnel occurred.

Subsequent investigations into the accident suggested that the decomposition was initiated by a solvent fire caused by a spark of unknown origin. Additional studies showed that any source of heat (>200°) could initiate the decomposition [e.g., hot flint spark, continued (10 sec) static spark, or flame]. Since this extremely rapid decomposition is self-propagating, a sample of any size held at room temperature will completely explode when any part

of the entire sample is subjected to flame or hot spark. The decomposition is characterized by instantaneous evolution of gas without significant flame resulting in a water-soluble black residue. Even if 1 is placed on filter paper at room temperature and exploded by a hot flint spark, little or no charring of the filter paper results. A test of the sodium salt of tetrazoleacetic acid (2) shows a similar violent decomposition that only could be initiated by flame. In both cases, the more pure the sample, the more violent the decomposition.

Further studies showed the parent tetrazoleacetic acid to have similar TGA and DTA data but to be much less sensitive to flame or hot spark. Similar other heterocycles³ and their corresponding potassium or sodium salts showed much less sensitivity to flame or hot spark.

Therefore, the potassium and sodium salts of tetrazoleacetic acid should be isolated with due caution and should be protected from any contact with high heat, flame, or hot spark. Additionally, any compound that is to be prepared in large quantities should be spark and flame tested to check sensitivity along these parameters.

Registry No.—1, 51286-83-0; 2, 51286-84-1.

References and Notes

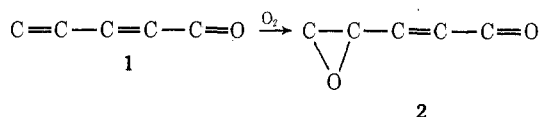
- (1) R. Raap and J. Howard, *Can. J. Chem.*, **47**, 813 (1969).
- (2) These analyses were performed by the Analytical Department of Eli Lilly and Co., Indianapolis, Ind.
- (3) Some of the heterocyclic systems analyzed were tetrazole, sodium tetrazole, 5-aminotetrazoleacetic acid and its potassium salt, and sydnoneacetic acid and its sodium salt. All of these compounds show similar thermal gravimetric data and differential thermal analyses but did show radically different combustion characteristics compared to the salts of tetrazoleacetic acid.

Communications

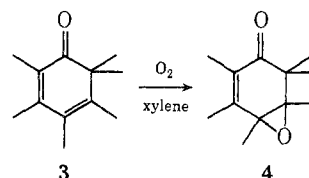
Synthetically Useful Epoxidations with Molecular Oxygen

Summary: Conjugated dienones and diene esters are epoxidized at the γ,δ double bond by molecular oxygen when heated in solvents which have readily abstractable hydrogen atoms.

Sir: We have found that the conversion 1 \rightarrow 2 occurs readily when compounds containing the moiety represented by



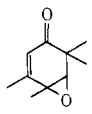
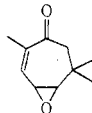
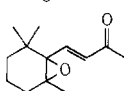
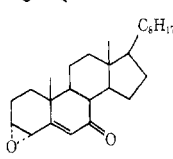
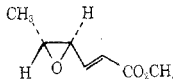
1 are heated in the presence of air or oxygen, in a solvent which has readily abstractable hydrogen atoms.¹ For example, when a xylene solution of dienone 3 was heated at 120–130° for 21 hr in the presence of air, epoxide 4² was formed in 65–75% yield. The reaction occurred at the



same temperature in cyclooctane (13 hr, 70–75%), mesitylene (14 hr, 80%), and cumene (8 hr, 90–95%), but in chlorobenzene no 4 was formed even after 48 hr. There is very little advantage in reaction time, yield, or reproducibility by bubbling air or oxygen through the reaction mixture; indeed, our experience thus far is that the yield of undesired side-products increases if the reaction is hurried in this way or by use of initiators. Experiments along these lines are, however, continuing.

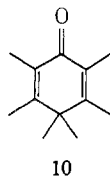
Table I lists several other epoxides which have been prepared by autoxidation of the corresponding unsaturated precursors. The reaction may be highly stereoselective. Thus with 3,5-cholestadien-7-one the product is the

Table I
Vinyl Epoxides Prepared Using Molecular Oxygen^a

Epoxide	No.	Yield, % ^b	Ref
	5	51	c, e
	6	52	d, e
	7	72	3
	8	31	4
	9	90	5

^a Xylene solvent, 120–130°, 24 hr. ^b No special attempt has been made to optimize yields. The reactions of 5–8 were performed on a 100-mg scale. When the oxidation of 9 was scaled up from 100 mg to 3 g, the yield improved from 49 to 90%. ^c Mp 48–50°. *Anal.* Calcd for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.20; H, 8.56. ^d *Anal.* Calcd for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.20; H, 8.50. ^e The structures were established by spectral data and independent synthesis using *m*-chloroperbenzoic acid.

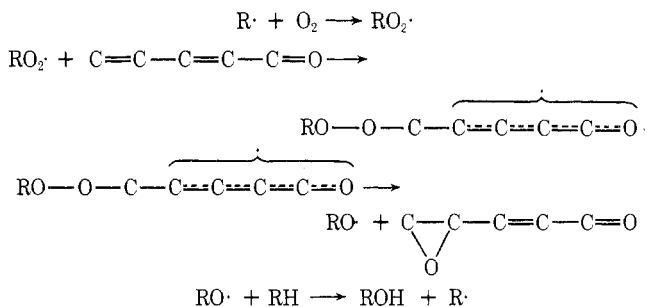
α -epoxide 8, and with methyl sorbate the *E,E* epoxide 9 was the predominant product (in the latter case, an nmr spectrum of the crude product showed traces of another isomer, probably *cis* at the epoxide ring). The products are usually similar to those obtained using *m*-chloroperbenzoic acid. However, isolated double bonds or singly conjugated systems (such as in 10) are not oxidized by



molecular oxygen, so that the method provides a selectivity not always available with a peracid. Thus an equimolar mixture of 3 and 10, heated in xylene for 24 hr, gave a

70% yield of 4 and essentially quantitative recovery of unreacted 10.

The oxidation probably involves a free radical mechanism of the following type.



The autoxidation may be initiated by reaction of triplet oxygen with the hydrocarbon solvent. Consistent with the above mechanism is the lack of oxidation in chlorobenzene and the formation of typical radical oxidation products from the solvent (*p*-methylbenzyl alcohol from xylene, cumyl alcohol and acetophenone from cumene, etc.).

Work on the mechanism and scope of the reaction is being continued.⁶

The following procedure is typical. A solution containing 1.0 mmol of 3 in 10 ml of xylene was heated at 120–130° in a flask equipped with a reflux condenser, for 24 hr. After removal of the solvent *in vacuo*, the residue was chromatographed on a Florisil column using 5% ether in hexane as the eluent, to afford 39 mg (22%) of recovered 3 and 115 mg (77%) of epoxide 4,² mp 48–49.5°.

Acknowledgement. We are indebted to the National Institutes of Health (GM 15997) for generous support.

References and Notes

- (1) The formation of epoxides on autoxidation of alkenes is, of course, well known; for a review, see F. R. Mayo, *Accounts Chem. Res.*, **1**, 193 (1968). However, because of competition between addition and abstraction processes and other factors, high yields suitable for the laboratory preparation of epoxides at high alkene conversions are rare (see, however, ref 6).
- (2) H. Hart, I. Huang, and P. Lavrik, *J. Org. Chem.*, **39**, 999 (1974).
- (3) P. Karrer and H. Sturzingar, *Helv. Chim. Acta*, **29**, 1829 (1946).
- (4) S. Akagi and K. Tsuda, *Chem. Pharm. Bull.*, **9**, 464 (1961).
- (5) Y. Suhara and T. Minami, *Bull. Chem. Soc. Jap.*, **39**, 1968 (1966).
- (6) While this work was in progress, a paper appeared [A. Padwa and L. Brodsky, *Tetrahedron Lett.*, 1045 (1973)] which describes a styrene epoxidation with molecular oxygen.

Department of Chemistry
 Michigan State University
 East Lansing, Michigan 48824

Harold Hart*
 Paul B. Lavrik

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