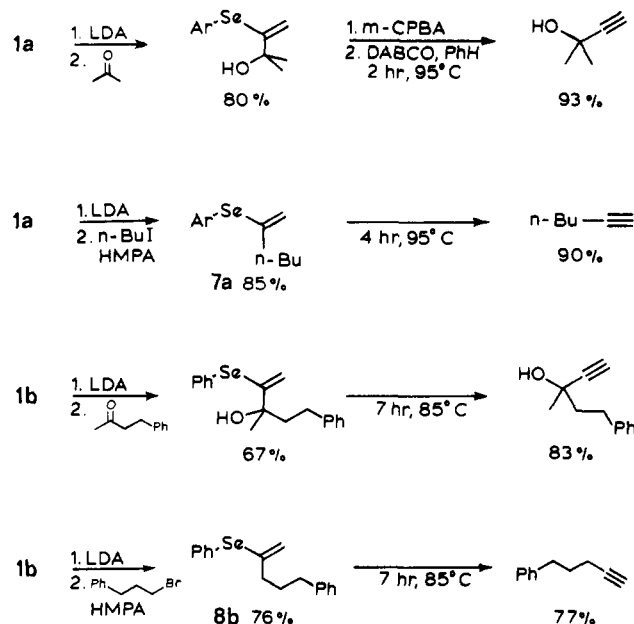


Scheme I



The observation, independently made by us,⁷ Raucher,⁸ and Krief,⁹ that some vinyl selenides can be deprotonated, coupled with the syn elimination reported here, allows α -lithio vinyl selenides¹⁰ to be used as lithium acetylide equivalents (see Scheme I, in which yields of the volatile acetylenes from **1a** were determined by NMR and those from **1b** were of isolated and purified materials).

Rough rate measurements show that the reactions follow first-order kinetics, with the following relative rates at 95 °C in benzene-*d*₆ (half-lives in brackets): **1a**, 1.0 (2.3 h); **1b**, 0.83 (2.8 h); **7a**-selenoxide, 9.7 (0.24 h); **3a**, 0.3 (7.4 h); **5a**, 5.4 (0.43 h); **6a**, 1.0 (2.3 h). The substituent effects are strikingly similar to those observed for syn elimination of aryl alkyl selenoxides.^{1a} Thus, substitution of a *m*-CF₃ group on the aryl ring (**1a** vs. **1b**) increases the rate by 1.3 while for the aryl ethyl selenoxides the rate is increased by 1.5. Replacement of the α hydrogen by methyl for alkyl selenoxides (i.e., ethyl vs. isopropyl selenoxide) increases the rate by 9.5 whereas factors of 10 (**1a** vs. **7a**, α -butyl) and 18 (**3a** vs. **5a**, α -methyl) are observed here. β substitution in alkyl selenoxides (i.e., propyl vs. isobutyl) retards the rate of elimination by 0.36; in the vinyl compounds (**1a** vs. **3a**), the rate is decreased by 0.3. The extent of allene formation which occurs for **5a** is also compatible with these rates: **6a** gives only allene with a relative rate of 1.0 whereas **5a** gives 15% of allene, with a partial rate for allene formation of 0.8. No allene was observed during the thermolysis of the selenoxides derived from **7a** and **8b**.³ These compounds lack the β -alkyl substituent of **5a** which retards acetylene formation.

A range of procedures is available for the preparation of vinyl selenides.^{1c,e,4,8,10,11} It seems likely that many of these can now be used to prepare acetylenes although the geometric requirements

for a syn elimination will limit the range of compounds that can be prepared. We have been able to find no other examples of acetylene-forming pericyclic eliminations involving sulfoxides and amine oxides, with the possible exception of a fragmentation involving a β -boron-substituted vinyl sulfoxide.¹² Enol acetates give acetylenes upon pyrolysis at 760 °C, but the mechanism does not appear to be a concerted cycloelimination.¹³ Other pyrolytic routes to acetylenes have been reported.¹⁴

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Hans J. Reich,* William W. Willis, Jr.

Samuel P. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin—Madison
Madison, Wisconsin 53706

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Low-Temperature Ozonation of Alkenes Adsorbed on Silica Gel

Sir:

The ozonation of compounds on silica gel has received considerable recent attention.¹⁻¹³ Particularly interesting reports include (i) regiospecific formation of tertiary alcohols from tertiary alkanes;^{1,3,5,11} (ii) formation of nitroalkanes in high yield from primary amines;⁴ (iii) carbon-carbon cleavage of alkanes;⁹ and (iv) high yields of α -carbonylation products from alkylcyclopropanes.^{6,7} This technique, called "dry ozonation", has been used to achieve carbonylation and epoxidation of triterpenes¹² as well as selective oxidation of the aromatic nucleus of arylalkanes.⁸

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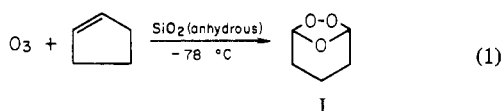
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The low-temperature ozonation of alkenes adsorbed on silica gel has not, to our knowledge, been investigated.¹³ We report here our results, which indicate that the product distribution and mechanism of ozonation of silica gel supported alkenes differ markedly from the course of ozonation in aprotic and nonparticipating solvents.¹⁴

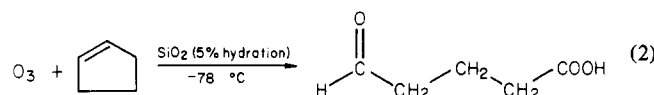
In general, the ozonation of 1,2-disubstituted alkenes in nonparticipating aprotic solvents under anhydrous conditions results in formation of monomeric ozonides, polymeric peroxides, and/or polymeric ozonides.¹⁴ By contrast, we find that ozonation of 1,2-disubstituted alkenes adsorbed on dried silica gel results in formation of virtually pure ozonides, and ozonation with water-containing silica gel results in double-bond scission with formation of equimolar amounts of carboxylic acid and aldehyde. Ozonation of simple unsubstituted cyclic alkenes with water-containing silica gel gives the expected aldehydic acid.

Ozonation¹⁵ of cyclopentene with silica gel vacuum dried at 300 °C results in formation of the normal monomeric ozonide (I)^{16,17} in high yield as the only product (eq 1). Some cyclopentene



is swept away in the gas stream, even at -78 °C, thereby lowering the yield. Nevertheless, the monomeric ozonide is isolated in excess of 80% yield. In contrast, normal ozonation of cyclopentene results in formation of mostly polymeric ozonide together with a low and highly concentration-dependent yield of monomeric ozonide.

We have also performed ozonation of cyclopentene adsorbed on silica gel loaded to a 5% water content (eq 2). Under these



conditions, we find that ozonation of cyclopentene results in oxidative cleavage of the double bond to give 5-oxopentanoic acid as the only major product; cyclopentene is completely consumed, and 5-oxopentanoic acid is formed in a yield exceeding 80%. Ozonation of cyclohexene on water-containing silica gel gave corresponding results, with 6-oxohexanoic acid formed as the major product. Ozonation of 1-methylcyclohexene under similar conditions gave 6-oxoheptanoic acid as the major product.

The ozonation to completion of 2-pentene supported on dried silica gel resulted in formation of the normal ozonide in a yield exceeding 90%.¹⁵ Ozonation of 2-pentene at -70 °C, either neat or in pentane solution, results in formation of cross ozonides, i.e., the ozonides of 2-butene and 3-hexene, as well as the ozonide of 2-pentene, in addition to acetaldehyde, propionaldehyde, and polymeric peroxidic material.¹⁸

Ozonation of *trans*-stilbene adsorbed on silica gel heated in air at 200 °C results in the formation of equimolar amounts of benzaldehyde and benzoic acid in high yield. Approximately 1% stilbene ozonide was detected under these conditions. Ozonation

of *trans*-stilbene with silica gel hydrated to approximately 5% water content gave benzaldehyde and benzoic acid as major products without detection of ozonide.¹⁹ Ozonation on silica gel vacuum dried at 300 °C gave *cis*- and *trans*-stilbene ozonides²⁰ as the only products.

Ozonation of alkenes in participating and generally protic solvents usually results in formation of α -oxyalkyl hydroperoxides.¹⁴ Ozonation in water results in formation of aldehydes or ketones and carboxylic acids, presumably because the intermediate hydroxyalkyl hydroperoxides are too unstable to permit isolation.²¹ It has long been recognized that acid-catalyzed decomposition of ozonides results in formation of aldehydes or ketones and carboxylic acids.²² Ozonides are also subject to rapid decomposition into aldehydes and carboxylic acids in dimethyl sulfoxide and dimethylformamide.²³

Ozonides have been routinely separated and purified by column chromatography on silica gel, and they are quite stable toward thermal decomposition.²⁴ It is therefore unlikely that surface silanol groups could effect the catalytic decomposition, at -78 °C, of ozonides. According to the well-established Criegee mechanism of ozonation, a primary ozonide dissociates into a carbonyl moiety and a carbonyl oxide zwitterionic species. Perhaps ozonation on a silica-gel surface containing adsorbed water results in immediate addition of a carbonyl oxide to surface water followed by rapid decomposition of the intermediate hydroxyalkyl hydroperoxide to a carboxylic acid and water, and, in effect, adsorbed water on a silica-gel surface acts in the same manner as a participating water solvent. In the absence of appreciable adsorbed water, recombination of adsorbed aldehyde and carbonyl oxide gives the normal ozonide, and for ozonation of unsymmetrical olefins, crossed ozonides do not occur because of restricted migration of adsorbed species on the silica surface. Vacuum drying of silica gel above 200 °C substantially removes physically adsorbed and hydrogen-bonded water,²⁵ and our results are consistent with this fact.

Potential synthetic advantages of silica gel supported ozonation of alkenes are (1) ozonation on dehydrated silica gel should permit high-yield formation of ozonides; (2) ozonation of unsymmetrical alkenes may be carried out without formation of cross ozonides; and (3) ozonation on hydrated silica gel permits high-yield double-bond scission, forming aldehyde or ketone and carboxylic acid functionality.

(19) Products were identified by comparison of VPC retention times and IR and NMR spectra with authentic samples. Benzoic acid was further identified by conversion to its methyl ester with diazomethane.

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Ivan E. Den Besten,* Thomas H. Kinstle

Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

Received February 14, 1980

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Intramolecular Electron-Transfer Induced Carbon-Hydrogen Bond Dissociation in Methyl-Substituted 1,10-Phenanthroline Complexes of Bis(η^5 -cyclopentadienyl)titanium

Sir:

Floriani and co-workers have found dicarbonylbis(η^5 -cyclopentadienyl)titanium(II) to be a useful reagent in numerous re-