Tetrahedron Letters,Vol.23,No.35,pp 3623-3626,1982 0040-4039/82/353623-04$03.00/0
Printed in Great Britain

OZONOLYSIS OF OLEFINS AND ACETYLENES ADSORBED ON SILICA GEL

Chaim Aronovitch, Daniel Tal and Yehuda Mazur*
Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

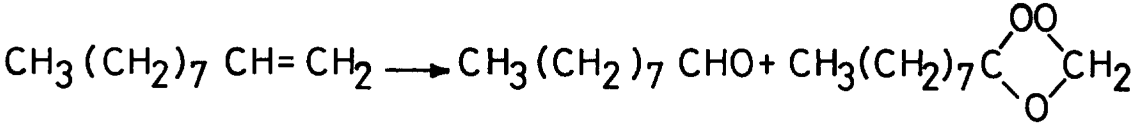
Abstract: Ozonation of phenyl ethylenes adsorbed on untreated silica gel results in aromatic aldehydes and on dried silica gel in ozonides and aldehydes. On the other hand ozonation of alkyl ethylenes on both types of silica gel results in a mixture of ozonides or polymeric peroxides similar to that obtained in aprotic solvents.

It has been recently claimed that ozonolysis of mono, di, or trialkyl, or aryl substituted olefins adsorbed on silica gel containing water results in the cleavage of their double bonds to give equimolar amounts of an acid and of a carbonyl compound, while the analogous ozonolysis on dry silica gel (heated in vacuum 300°C) gives solely ozonides.[1]

We have also performed the ozonolysis of a number of olefins adsorbed on silica gel (a) untreated (Merck, Kieselgel 60, 70-260 mesh), (b) containing additional 5% of water, and (c) preheated to 300°C in vacuum, and obtained different results. The reactions were performed by passing ozone (3%, in oxygen) at -78° through the silica gel containing preadsorbed olefin (2% w/w). The products were isolated by solvent elution after removal of the excess of ozone with a stream of nitrogen at the same temperature.[2]

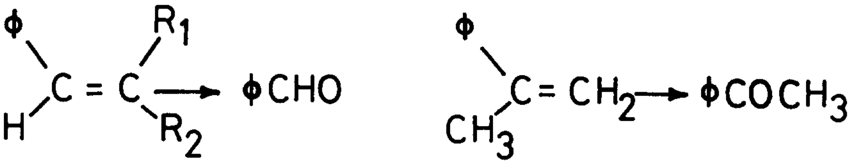
The reactions with ozone were very fast, and after a short time period (ca. 2-5 minutes) the conversions were complete. The analysis of the reaction products was performed immediately at the termination of the reactions since ozonides and peroxides formed may decompose on standing to yield aldehydes and acids.[3,4]

We have found that 1-decene, cis-6-dodecene, and 1-methylcyclohexene adsorbed on any of the three types of silica gel were converted with ozone to ozonides (75-85%) and aldehydes (nonanal, hexanal and 6-oxohexanal, respectively) (10-20%), while cyclohexene gave mainly polymeric peroxide (80-90%) and adipic aldehyde (10-20%). The results show a marked similarity with ozonation in nonparticipating aprotic solvents.[3,5]



Under the reaction conditions, the yields of acids were negligible. However, after longer reaction periods larger quantities of acids were formed as a result of either oxidations of the aldehydes[6] or decompositions of the ozonides or peroxides.[3,4]

Ozonolysis of phenylethylenes adsorbed on untreated silica gel takes a different course from the ozonolysis of the other olefins, yielding almost exclusively aromatic aldehydes or ketones. Thus, styrene and its β-derivatives cis and trans stilbene and trans β-ethylstyrene gave in almost quantitative yield benzaldehyde,[7] while α-methylstyrene gave acetophenone.

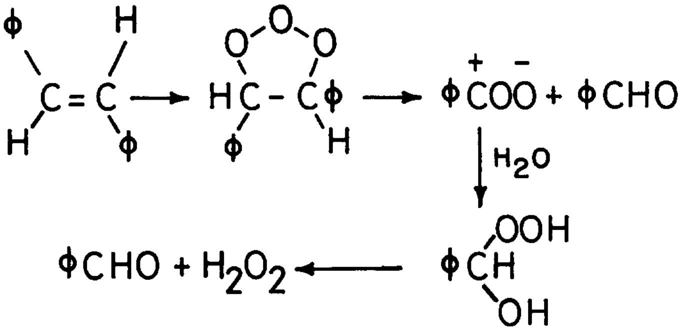


$R_1 = R_2 = H$; $R_1 = \phi$, $R_2 = H$

$R_1 = H$, $R_2 = \phi$; $R_1 = H$, $R_2 = Et$

On the other hand, ozonolysis of these compounds on dry silica gel resulted in mixtures consisting of benzaldehyde (or acetophenone) and corresponding ozonides formed in similar ratios to ozonations in aprotic solvents.[8]

We assume that in the ozonations on silica gel the adsorbed water causes the exceptional behaviour of phenylethylenes, since it reacts with the intermediate α-phenyl-substituted carbonyl oxides to give hydroxy hydroperoxides.[9] Hydrolytic decomposition of the latter results in aromatic aldehydes or ketones and hydrogen peroxide. A similar mechanism was suggested previously to explain the formation of aldehydes in the ozonolysis of some polycyclic aromatic compounds.[10]

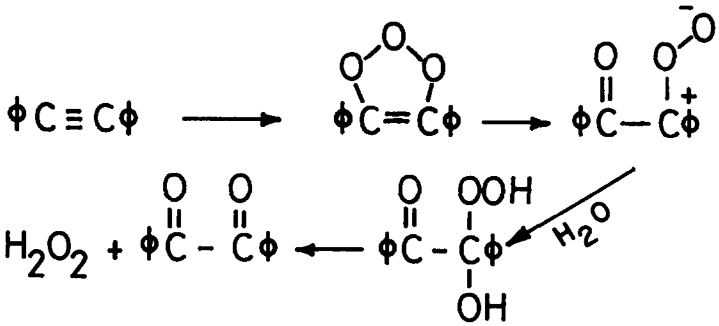


It thus appears that the intermediate phenylsubstituted carbonyl oxides are more reactive towards nucleophilic attack of water than the alkyl substituted carbonyl oxides. The latter compounds do not react under these conditions with water, but rather react with the intermediate carbonyl compounds to give ozonides or polymerize to give oligomeric peroxides. An additional reason for the absence of ozonides is the comparatively lower reactivity of benzaldehyde with the carbonyl oxides in a dipolar cycloaddition reaction.[11]

We have observed that also ozonation of tetramethylethylene adsorbed on silica gel (untreated or containing an additional 5% water) does not lead to normal ozonation products,[12] but mainly to acetone (95%). We may thus assume that also in this case water plays a role leading to hydroxy-hydroperoxide, which decomposes giving acetone. Analogous formation of acetone was observed previously on ozonation of tetramethylethylene in methanolic or ethanolic solution followed by treatment with water.[13]

We have also ozonized a number of acetylenes including diphenylacetylene, 2-methyl-1-heptyne, ethynylbenzene and 1-hexyne adsorbed on untreated silica gel. In all cases except the first one we have observed "normal" behaviour; i.e., the formation of mixtures of acids (formed by hydrolysis of the respective anhydrides on silica gel) and carbonyl compound.[14] Diphenylacetylene gave only one product, the diketone benzil.

This anomaly is in accord with our assumption that carbonyl oxide derivatives α-substituted with a phenyl ring react preferentially with water to give hydroperoxides which are the precursors of α-diketones.



We assume that the reaction of ozone with other acetylenes results in carbonyl oxide derivatives which do not react with water, but rearrange instead to give the normal ozonation products.

The use of silica gel as a matrix for the ozonolysis of phenylethylenes and tetrasubstituted olefins has synthetic advantages since aldehydes or ketones are formed in high yield without the necessity of using reducing agents.

References and Notes

1. Den Besten,I.A. and Kinstle, T.H., J.Amer. Chem. Soc., 1980, 102, 5968.
2. The experimental procedure was similar to that described before; cf.: Cohen, Z., Varkony, T.H., Keinan, E. and Mazur, Y., Org. Synth., 1980, 59, 176; except that the excess of ozone was removed at -78°C. The reactions were performed with 25 g silica gel containing 0.5 g substrates.
3. Bailey, P.S.: "Ozonation in Organic Chemistry", Vol. I, Academic Press, New York, 1978, pp. 83-89.
4. Henne, L., and Perilstein, W.L., J. Amer. Chem. Soc., 1943, 65, 2183; Criegee, R., Kerckow, A. and Zinke, H., Chem. Ber., 1955, 88, 1879; Fliszar, S. and Chylinska, J.B., Canad. J. of Chem., 1968, 46, 783.
5. Murray, R.W. and Williams, G.J., J. Org. Chem., 1969, 34, 1891; Criegee R., J. Liebieg Ann. Chem., 1953, 583, 1.
6. White, H.M. and Bailey, P.S., J. Org. Chem., 1965, 30, 3037; Erickson, R.E., Bakalik, D., Richardson, C., Scanlon, M. and Huddleston, G. J. Org. Chem., 1966, 31, 461.
7. In addition, propionaldehyde was isolated from β-ethylstyrene.
8. Thus styrene on dry silica gel gave ca. 65% while cis stilbene ca. 30% of the corresponding ozonides in addition to benzaldehyde. For ozonolysis of phenylethylene in aprotic solvents cf. Criegee, R., Korber, H. and Grand, D., Adv. Chem. Ser., 1971, 112, 22 and Fliszar, S., Gravel, D. and Cavalier, E., Canada. J. of Chem., 1966, 44, 235.
9. Benzaldehyde is formed in high yield on ozonolysis of phenylethylene in solution containing methanol followed by treatment with water, cf. Subluskey, L., Harris, G.C., Maggiolo, A. and Tumolo, A.L., Adv. Chem. Ser., 1959, 21, 149.
10. Sturrock, M.G., Cline, E.L. and Robinson, K.R., J. Org. Chem., 1963, 28, 2340; Sturrock, M.G., Cravy, B.J. and Wing, V.A., Canada. J. of Chem., 1971, 49, 3048; Bailey, P.S. and Ashton, J.B., J. Org. Chem., 1977, 22, 98; Bailey, P.S., Kolsaker, P., Sinha, B., Ashton, J.B., Dobinson, F. and Baterbee, J.E., J. Org. Chem., 1964, 29, 1400; Sturrock, M.G. and Duncan, R.A., J. Org. Chem. 1968, 33, 2149.
11. Bailey, P.S., Chem. Rev., 1958, 58, 925; Keul, H., Chem. Ber., 1975, 108, 1207.
12. Criegee, R., Bath, S.S. and von Borhaupt, B., Chem. Ber., 1960, 93, 2891.
13. Nebel, C., Chem. Commun., 1969, 101.
14. DeMore, W.B., ed. Lin, C.C. J. Org. Chem., 1979, 38, 985; Criegee, R. and Lederer, M., Ann. Chem., 1953, 583, 29; Bailey, P.S., Chang, Y. and Kwie, W.W.L., J. Org. Chem., 1962, 27, 1198.

(Received in UK 14 June 1982)