BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(4), 1337—1338 (1975)

Catalytic Transformation of Cyclohexene Hydroperoxides to Epoxy Alcohols with Vanadyl Acetylacetonate

Takashi Itoh, Kiyotomi Kaneda, and Shiichiro Teranishi
Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

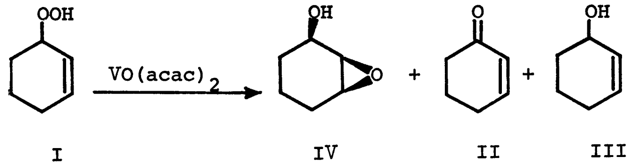
(Received November 5, 1974)

Synopsis. Cyclohexene hydroperoxide and its methyl derivatives undergo rearrangement in the presence of the vanadyl acetylacetonate catalyst to the corresponding epoxy-alcohols with high *cis*-stereoselectivity in high yields.

Hydroperoxide decomposition with transition metals can be classified mainly into homolytic decomposition (Fe, Co, Cu catalysts)1) and heterolytic decomposition (Mo, V, W catalysts).2) Rhodium complexes catalyze the homolytic decomposition of cyclohex-2-enyl hydroperoxide (I) to cyclohex-2-en-1-one (II) and cyclohex-2-en-1-ol (III).3) Little information is available on the heterolytic decomposition of cyclohexene hydroperoxides.

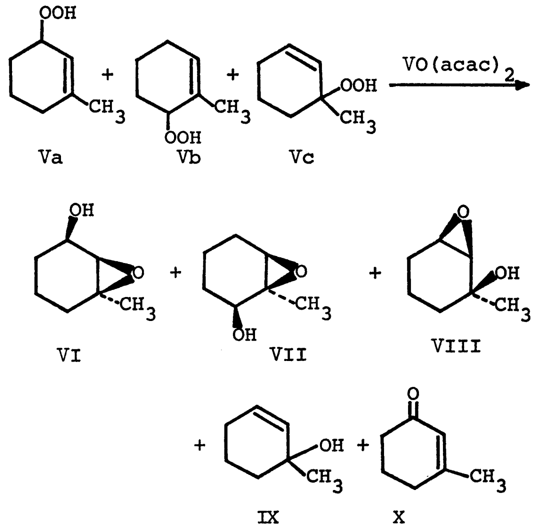
We wish to report the selective transformation of cyclohexene hydroperoxides with the $VO(acac)_2$ catalyst into *cis*-epoxy-alcohols.

The reaction of cyclohex-2-enyl hydroperoxide (I) with $VO(acac)_2$ was carried out in benzene with stirring under nitrogen atmosphere at 40 °C. After 4 hr, glc analysis of the resulting solution revealed that the main product was 2,3-epoxy-cyclohexanol (IV) (79% yield based on consumed peroxide) accompanied by a small amount of the usual decomposition products (II (8%) and III (5%)). The stereochemistry of this epoxy-alcohol was assigned to *cis*-configuration by IR and NMR spectra.4) The presence of *trans*-isomer could not be detected by glc analysis.

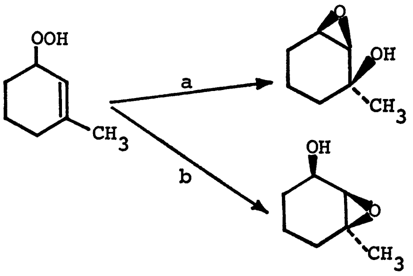


In order to ascertain the generality of this reaction and to clarify the stereochemistry of the rearrangement, hydroperoxides from an unsymmetric olefin were also investigated. Thus, a mixture of three hydroperoxides from 1-methylcyclohexene, containing 3-methylcyclohex-2-enyl hydroperoxide (Va) (51%), 2-methylcyclohex-2-enyl hydroperoxide (Vb) (34%) and 1-methylcyclohex-2-enyl hydroperoxide (Vc) (15%), was treated with $VO(acac)_2$ under the same conditions. The main products were three epoxy-alcohols, 3-methyl-*cis*-2,3-epoxycyclohexanol (VI) (46%), 2-methyl-*cis*-2,3-epoxycyclohexanol (VII) (24%) and 1-methyl-*cis*-2,3-epoxycyclohexanol (VIII) (1%).

The structures of the three epoxy-alcohols were assigned by comparison of their NMR and IR spectra and retention times with those of authentic samples prepared by the $VO(acac)_2$ catalyzed epoxidations of the corresponding methylcyclohexenols with *t*-butyl hydroperoxide.5) *cis*-Configurations of these epoxy-alcohols were further confirmed by the reductive opening of epoxide rings with $LiAlH_4$ to the corresponding *cis*-diols.6)



The product distribution of the above reaction showed that peroxides Va, Vb and Vc were transformed into epoxy-alcohols VI, VII and VIII, respectively. This indicates that the transformation follows reaction pattern b rather than pattern a.7)



Scheme 1.

Thus, $VO(acac)_2$ catalyst can transform cyclohexene hydroperoxides selectively into epoxy-alcohols with a high *cis*-stereoselectivity (*cis*-isomer>99%). $V(acac)_3$ gave lower yields and selectivity. The molybdenum analogue $MoO_2(acac)_2$ was found to be a poor catalyst.

Equimolar reaction of cyclohexene hydroperoxide and $VO(acac)_2$ gave II (25%), III (63%) and a trace amount of IV. ESR study showed that the addition of hydroperoxide (I) to the benzene solution of $VO(acac)_2$ (molar ratio 1 : 1—5 : 1) causes a large reduction (85—90%) in the strength of the V^{IV} signal and no new other signals appeared. Thus, it seems that $VO(acac)_2$ can be oxidized with hydroperoxide to higher valence species (V^V), which might act as an actual catalyst for the formation of epoxy-alcohols.

Experimental

Materials. Cyclohexene hydroperoxides, I and V, were prepared as reported previously.[3] The purity was determined by iodometric titration;[8] I (86%) and V (87%). Impurities found were the corresponding cyclohexenols and cyclohexenones. The isomer distribution of hydroperoxides (V) was determined by the area ratios of signals of vinylic protons and hydroperoxy protons in NMR spectrum.

Reaction of I. Peroxide I (10 mmol) in 5 ml dry benzene solution was added dropwise to a 25 ml dry benzene solution of VO(acac)$_2$ (0.1 mmol) at 40 °C under nitrogen atmosphere with stirring. After 4 hr, 98% of I was consumed. Three products were found by glc analysis (OV 17 at 80 °C); IV (7.7 mmol), II (0.8 mmol) and III (0.5 mmol). These compounds were identified by comparison of their NMR and IR spectra and retention times with those of authentic samples.[3,4]

Fractional distillation under reduced pressure gave IV (0.65 g); bp 86 °C/6 mmHg (Ref.,[4] 100—102 °C/12 mmHg).

Reaction of V. The same procedure as for I was used. Three epoxy-alcohols were obtained as the main products by glc analysis (PEG 6000 at 120 °C); VI (4.5 mmol), VII (2.4 mmol) and VIII (0.1 mmol). VI; IR (neat) 3400, 1092, 1034, 888 and 839 cm^{-1}. NMR (CCl$_4$) τ 6.13 (m, 1H), 7.00 (d, 1H), 7.9—8.8 (m, 6H) and 8.69 (s, 3H). VII; IR (neat) 3400, 1041 and 835 cm^{-1}. NMR (CCl$_4$): τ 6.32 (m, 1H), 6.96 (t, 1H), 7.8—8.7 (m, 6H) and 8.62 (s, 3H). VIII; IR (neat) 3400, 1143, 1100, 1087, 930, 857 and 820 cm^{-1}. NMR (CCl$_4$): τ 6.70 (m, 1H), 7.09 (d, 1H), 7.7—8.8 (m, 6H) and 8.66 (s, 3H). The usual decomposition products, methylcyclohexenols and methylcyclohexenones, *e.g.*, IX (0.8 mmol) and X (0.5 mmol), were minor products.

LiAlH$_4$ Reduction of Epoxy-alcohol to cis-*Diol.* VII was separated by preparative glc and then 1.0 mmol of VII was treated with 2.5 mmol of LiAlH$_4$ in 10 ml dry ether. From ethyl acetate extract of the reaction mixture, white crystals of 1-methylcyclohexane-*cis*-1,2-diol (0.08 g, 0.6 mmol) were obtained; mp 68.0—68.5 °C (Ref.,[9] 68.5 °C). NMR (C$_2$D$_5$OD): τ 5.60 (m, 1H), 8.1—8.8 (m, 8H) and 8.84 (s, 3H).

References

1) For a recent review see, G. Sosnovsky and D. J. Rawlinson, in "Organic Peroxides" D. Swern, ed., Vol. 2, Wiley-Interscience, New York, N.Y. (1971), pp. 157—191.

2) R. A. Sheldon and J. A. Van Doorn, *J. Catal.*, **31**, 427 (1973) and references cited therein.

3) K. Kaneda, T. Itoh, Y. Fujiwara, and S. Teranish, This Bulletin, **46**, 3810 (1973).

4) P. Chamberlain, M. L. Roberts, and G. H. Whitham, *J. Chem. Soc., B*, **1970**, 1374.

5) K. B. Sharpless and R. C. Michaelson, *J. Amer. Chem. Soc.*, **95**, 6136 (1973).

6) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, **1957**, 1958.

7) Detailed mechanism, in particular the discrimination between intramolecular rearrangement and intermolecular epoxidation, is not clear at present but it can be said that the epoxidation takes place at olefinic double bonds of the starting hydroperoxides.

8) V. R. Kokatnur and M. Jelling, *J. Amer. Chem. Soc.*, **63**, 1432 (1941).

9) C. A. Bunton and M. D. Carr, *J. Chem. Soc.*, **1963**, 770.