(methylsulfonyl)-5-nitropyrimidine[15] were synthesized as described in literature. The ^{15}N NMR spectra were recorded at 30.408 MHz in 15-mm o.d. sample tubes on a Bruker CXP-300 spectrometer equipped with a B-UT 100 variable-temperature controller. For measurements in liquid ammonia, thick wall tubes we reused. In all cases the tubes contained an internal 4-mm capillary containing a 2% solution of $CH_3{}^{15}NO_2$ in CD_3OD. This was used both for the lock signal and as external standard. The chemical shift of CH_3NO_2 in methanol-d_4 (CH_3NO_2/CD_3OD) was 1.97 ppm upfield from pure nitromethane. The latter has a chemical shift of 380.23 ppm downfield from liquid ammonia[16] (δNH_3). The nitrogen chemical shifts measured against nitromethane in the capillary were then converted to liquid ammonia using the following expression:

$$\delta NH_3 = \delta CH_3NO_2/CD_3OD + 378.26 \text{ ppm}$$

Normally the ^{15}N spectra were taken of 0.2–1.0 M solutions. In the DEPT pulse sequence the 90° pulse width for ^{15}N and ^{1}H was 45 μs and 32 μs, respectively, and the delay between the cycles was 3 s. Typical values for the proton-coupled spectra were a pulse width of 15 μs (30°) for ^{15}N and repetition time of 3 s. The spectral width was 4 kHz (0.24 Hz/point) for **1a–d** in chloroform and/or dimethyl sulfoxide and 15 kHz (0.92 Hz/point) for the measurements in liquid ammonia.

Registry No. **1a**, 14080-32-1; **1b**, 15579-58-5; **1c**, 14001-70-8; **1d**, 65735-65-1; **2a**(A), 84928-78-9; **3a**(B), 84928-80-3; **3c**(A), 84928-82-5; **3d**(A), 84928-84-7; ^{15}N, 14390-96-6; NH_3, 7664-41-7.

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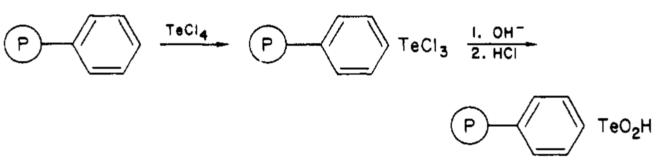
Communications

A Site Isolated Tellurium Oxidation Catalyst Having No Soluble Analogue

Summary: Although other organotellurium compounds have no activity as oxidation catalysts, cross-linked polystyrene tellurinic acid catalyzes the selective epoxidation of olefins with hydrogen peroxide.

Sir: Oxidations catalyzed by tellurium compounds, except for those involving molecular oxygen,[1] are unknown. This is unexpected since there are many examples of oxidation catalysis involving both inorganic[2] and organoselenium compounds.[3] We have been interested in the use of peroxides as selective oxidizing agents and have prepared a catalyst containing tellurium bonded to polystyrene which allows the quantitative epoxidation of olefins with H_2O_2. Similar catalysts having anchored functional groups containing Mn,[4] As,[5] and Se[6] have been reported for H_2O_2 oxidations, but for each catalyst low molecular weight analogues were known to be active.

The anchored tellurium catalyst is readily prepared by condensation of $TeCl_4$ with divinylbenzene–styrene copolymer followed by hydrolysis of the (trichlorotelluro)arene product. Such condensations have been used



for the preparation of arenetellurinic acids which, however, have no catalytic activity.[7] In a typical oxidation, 1 g of solid catalyst prepared from XAD-2 resin is stirred with 20 mL of 1.0 M cyclohexene and 1.0 M H_2O_2 in *tert*-butyl alcohol or dioxane at 60 °C for 24 h to produce a quantiative yield of cyclohexene oxide, based on either reagent. Reaction solutions prepared from 30% H_2O_2 and containing as much as 12% H_2O produce no diol.

Table I. Epoxidation of Olefins with H_2O_2[a]

olefin	rel rate[b]
1-methylcyclohexene	54
cyclohexene	21
3-methylcyclohexene[c]	21
trans-2-butene[d]	15[e]
styrene	10[e]
cis-2-octene[f]	4.3
trans-2-octene[g]	4.2
1-octene	1.0
allyl chloride	0.66[e]
allyl alcohol	0.13 (0.21)[h]

[a] 60 °C, 2 g of catalyst/20 mL of dioxane. [b] By comparison to cyclohexene ($k_2 = 1.03 \times 10^{-5}$ L mol^{-1} s^{-1}) using the same XAD-2 supported catalyst unless otherwise noted. [c] 3-Methylcyclohexene oxide is produced with cis:trans = 38:62 compared to 54:46 for *m*-chloroperbenzoic acid. [d] Produces *all-trans*-2,3-butane oxide. [e] Using XAD-4 supported catalyst, $k_2 = 12 \times 10^{-5}$ L mol^{-1} s^{-1}. [f] Produces *all-cis*-2,3-octane oxide. [g] Produces *all-trans*-2,3-octane oxide. [h] By competitive rate experiment with cyclohexene.

A study of the reaction kinetics in dioxane shows the oxidation to be cleanly first order in olefin and in H_2O_2 concentration, the rate being directly proportional to the amount of catalyst used. The kinetic behavior holds over a wide range of concentrations and, in fact, may be used to predict the approximate rate of epoxide formation when the reaction solution is passed through a fixed catalyst bed (646 g/L).

The effect of olefin structure on the oxidation rate, shown in Table I, is the same as that found with other electrophilic reagents such as peracids[8] or hydroperoxides;[9] increasing alkyl substitution accelerates the rate. The oxidation is stereospecific, cis–trans geometry being retained in the epoxide product. Results with 3-methylcyclohexene indicate that attack on the least hindered side of the double bond is favored. Allyl alcohol is unexpectedly

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unreactive and demonstrates an effect already observed when a polar substrate must react at a catalytic site in the nonpolar environment of the polystyrene surfaces.[10]

Catalyst activity depends strongly on the degree of cross-linking in the divinylbenzene–styrene copolymer from which it was prepared. For example, catalyst from 1%, 8%, and 20% (XAD-2) cross-linked polystyrene gave conversions of 2.6%, 7.6%, and over 50%, respectively. On the other hand, the amount of tellurium which can be introduced into these catalyst is inversely proportional to the cross-linking, being 28%, 24%, and 4.3% by weight. Catalysts prepared from, XAD-4, the most highly cross-linked resin commercially available, are the most active[11] and are preferred for synthetic work since they may give rates up to 10 times faster than catalysts prepared from XAD-2. The physical properties of catalysts closely resemble the resin from which they were made and change little with use.

The lack of catalytic activity of soluble tellurinic acids was confirmed by the preparation of phenethyl tellurinic acid and anisyl tellurinic acid.[12] They were found to be inactive under typical epoxidation conditions. Dimethyl ditelluride and diphenyl ditelluride, which may be regarded as precursors for tellurinic acids assuming that H_2O_2 acts upon them as it does upon diselenides,[13] also were tested and found to be inactive. Two obvious explanations for the activity of the tellurated resin are proposed:

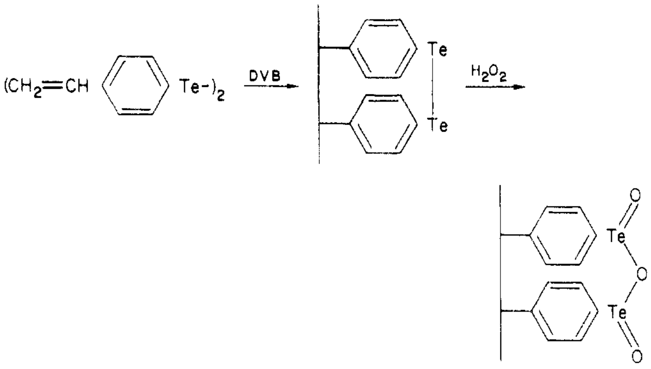
1. Various tellurium derivatives, formed in the preparation of the catalyst and present as bonded groups or absorbed byproducts, possibly may be very active epoxidation catalysts. These can form, for example, by reaction at the free vinyl group in the resin or by condensations involving adjacent phenyl groups.

2. Tellurinic acids may be active epoxdation catalysts but exist largely as anhydrides even in aqueous solutions as may be inferred from the reported[14,15] preparation of either acid or anhydride by careful acidification of solutions of their sodium salts. Equilibration would be influenced by the polymer matrix.

For evaluation of the first supposition, the following reference compounds were tested for catalytic activity under typical epoxidation conditions: TeO_2, diphenyl telluride, phenyltelluropolystyrene,[16] and diphenylenetellurone.[17] Tellurides are precursors for telluroxides[7] which conceivably may be oxidizing agents by analogy to selenoxides. Since the heavy cross-linking of the polymeric catalyst is a requirement for activity, the rigid telluroxide, diphenylenetellurone was used as a model. None of the compounds demonstrated any activity, making it improbable that the active catalytic site involves a functional group other than an aromatic tellurinic acid or a derivative.

Additional experiments cast some doubt on the assumption that the prevention of anhydride formation is responsible for the activity of the polymer. When oxidations are conducted with the polymeric catalyst in the presence of added excess anisyl tellurinic acid, no diminution of the epoxidation rate occurs. Formation of a mixed anhydride could occur under these conditions.

Polymers are now being prepared in which the tellurinic acid groups are placed in the polymer matrix by a template technique so that interaction of two groups is sterically favored. This was accomplished by copolymerizing bis(*p*-vinylphenyl) ditelluride[18] with divinylbenzene and treating the polymer with H_2O_2 to oxidize the ditelluride linkage to form fixed neighboring tellurinic acid groups.



Initial work produced a polymer with catalytic activity comparable to a tellurated XAD-2 resin. On the other hand, copolymerization of *p*-vinylbenzenetellurinic acid with divinylbenzene produced a polymer with randomly placed acid groups. It displayed little activity. In view of this, it may be postulated that anhydride formation is in fact required and sufficiently favored only in the solid catalyst. This may represent an example where the steric effect of a rigid support lowers the entropy of activation and enhances the formation of what would in solution be the less favored active form of the catalyst. Epoxidation of olefins may occur through reaction of peroxy intermediates formed from H_2O_2 and tellurinic anhydride in a manner similar to that demonstrated for carboxylic peracids.

Registry No. $TeCl_4$, 10026-07-0; XAD-2, 37380-42-0; XAD-4, 9060-05-3; bis(4-vinylphenyl)ditelluride, 100351-42-6; (bis(*p*-vinylphenyl)ditelluride)·(divinylbenzene)copolymer, 100351-43-7; 1-methylcyclohexene, 591-49-1; cyclohexene, 110-83-8; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; 1-octene, 111-66-0; 3-methylcyclohexene, 591-48-0; *trans*-2-butene, 624-64-6; styrene, 100-42-5; allyl chloride, 107-05-1; allyl alcohol, 107-18-6; cyclohexene oxide, 286-20-4; divinylbenzene, 1321-74-0.

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Stereochemical Transcription via the Intramolecular Diels–Alder Reaction. Enantioselective Synthesis of the Nucleus of (+)-Pillaromycinone

Summary: Synthesis of a tetracyclic structure containing functionality and stereochemistry similar to that of (+)-pillaromycinone has been accomplished from L-(+)-rhamnose, using an intramolecular Diels–Alder reaction

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