nitrogen and sulfur. The rings which contain these heteroatoms may oxidize to the correspondig *N*-oxide or sulfone. It may be possible to isolate and characterize these units. The remarkable stability of the *N*-oxides of pyridine and quinoline as well as dibenzothiophene sulfone give an indication that these general structure types should survive a TFA/H_2O_2 coal oxidation if indeed they are actually present in this material. Accordingly, direct evidence for heteroatom distribution in coal could be available.

Experimental Section

General Conditions. Trifluoroperacetic Acid. The reagent was prepared by the dropwise addition of 30% aqueous hydrogen peroxide[8] to trifluoroacetic acid (TFA) at 0 °C. The final solution contained no more than 10% water.[9] The ice bath was removed after the peroxide addition was complete. The material to be oxidized was added slowly with stirring to the trifluoroperacetic acid solution. The reaction mixture heated up while the addition of the material continued. The rate of addition was maintained such that the exothermicity of the reaction was controlled. An efficient reflux condenser was mounted on the flask and connected to a carbon dioxide trap (an aqueous solution of barium hydroxide). The barium carbonate produced in this way was decomposed by hot concentrated hydrochloric acid solution. The liberated carbon dioxide was collected in an ascarite trap. This precautionary analysis revealed that the carbon dioxide content of the white precipitate was between 91 and 97% of the theoretical value for pure barium carbonate. Any gas which passed through the CO_2 trap was collected for mass spectral analysis. The composition of the reaction solution was determined periodically throughout the course of the reaction. Minute samples (1 μL) were removed via syringe (through a sidearm equipped with a septum) and analyzed by gas chromatography. Tentative peak assignments were made by coinjections with authentic samples. The workup procedure employed was essentially the same as that described previously[3] except that no ester derivatives were prepared. Instead, the reaction products (free acids) were analyzed on two different columns: 10% SP1200 and 10% SP2300, both 1% phosphoric acid, 6 ft × 0.25 in, and 80/100 mesh of Supelcoport.

The mass spectral data were obtained from a Du Pont 21-490 magnetic-focusing mass spectrometer after the reaction components had been separated on one of the gas chromatographic columns.[10]

Instability of the Reagent. The solution of hydrogen peroxide and trifluoroacetic acid is not stable. The decomposition is greatly facilitated by inorganic chemicals. In one experiment 6.6 mL of 30% H_2O_2 was added to 50 mL of trifluoroacetic acid as previously described. A crystal of cuprous chloride was then added; after 3 h, 13.0 mmol of CO_2 had been produced. The gas which passed through the barium hydroxide solution was collected, and mass spectral analyses revealed the presence of fluoroform (CHF_3).

Complete Oxidation of Substrate. Typical Reaction Stoichiometry. The general reactions were employed to effect complete oxidation. The trifluoroperacetic acid solution was prepared by the dropwise addition of 30% H_2O_2 (10.0 mL, 88 mmol) to trifluoroacetic acid (75.0 mL) at 0 °C. The ice bath was removed and *n*-propylbenzene (0.60 g, 5.0 mmol) added slowly. The reaction time was 2 h. Analysis by gas chromatography revealed there were two products, butyric acid (82%) and acetic acid (18%). The results of the other reactions are summarized in Table I.

Incomplete Oxidation of Substrate. The general reaction conditions previously described were followed with the following exceptions. A cold-water bath was used to maintain lower temperatures during the course of the reaction, and the stoichiometric ratio of the peroxide to substrate was lower from almost 18:1 to 8:1.

Acknowledgment. The authors wish to express their appreciation to Professor N. C. Deno and M. L. Gorbaty for their helpful counsel during the course of this work.

Registry No. Toluene, 108-88-3; *n*-propylbenzene, 103-65-1; *n*-pentylbenzene, 538-68-1; *o*-xylene, 95-47-6; hexamethylbenzene, 87-85-4; acenaphthene, 83-32-9; pyridine, 110-86-1; quinoline, 91-22-5; dibenzothiophene, 132-65-0; acetic acid, 64-19-7; butyric acid, 107-92-6; hexanoic acid, 142-62-1; pentanoic acid, 109-52-4; succinic acid, 110-15-6; pyridine *N*-oxide, 694-59-7; quinoline *N*-oxide, 1613-37-2; dibenzothiophene sulfone, 1016-05-3; trifluoroperacetic acid, 359-48-8.

(8) Standardization of hydrogen peroxide solutions was accomplished by refractive index. See P. A. Giguere and P. Geoffrion, *Can. J. Res., Sect. B*, **27**, 168 (1949).

(9) If a larger amount of water is used, the oxidation of aromatic hydrocarbons is inhibited, N. C. Deno, private communication.

(10) Mass spectral data was obtained by Gollob Microanalytical Co., Berkeley Heights, NJ.

Multiple Extrusion Methods for the Preparation of Sterically Hindered Olefins. An Approach to Tetra-*tert*-butylethylene

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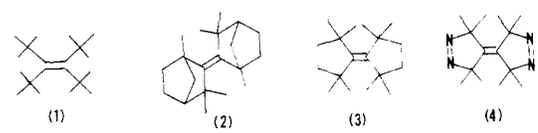
While twofold extrusion procedures have proved to be very useful in the preparation of very sterically hindered olefins, the extremely hindered tetra-*tert*-butylethylene (**1**) has remained elusive. An approach to **1** based on "tied-back" intermediates such as the selone **13** and diazo compound **14** was investigated. Although 1,1-diphenyl-2,2-di-*tert*-butylethylene (**16**) could be prepared by a combination of twofold extrusion and reductive cleavage, no significant formation of **1** could be detected by using analogous procedures, the major product being the azine **18**. Reaction of **14** with selenofenchone directly gave 2,2′-bifenchylidene (**2**) as the only olefinic product.

Approaches to the synthesis of very sterically hindered olefins and investigations of the chemical and physical properties of these compounds have recently attracted much attention.[1] These investigations may prove very useful in understanding the nature of sterically hindered environments. In this area the ultimate synthetic goal of a number of research groups is the extremely hindered tetra-*tert*-butylethylene (**1**)[2-5] (Chart I).

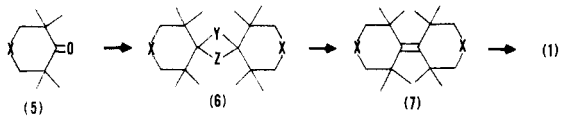
Chart I



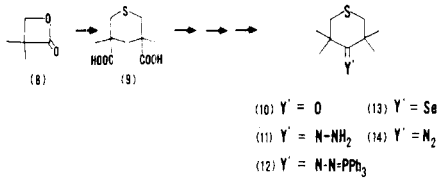
(1) For recent reviews, see: (a) T. T. Tidwell, *Tetrahedron*, 1855 (1978); (b) J. F. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976).

0022-3263/80/1945-2890$01.00/0

Scheme I



Scheme II



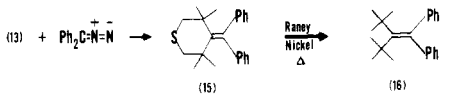
While this compound has remained elusive, very sterically hindered olefins which closely approximate the steric hindrance of 1 have been prepared by the use of "twofold extrusion" reactions. *syn*-2,2'-Bifenchylidene[4] (2) and bi-2,2,5,5-tetramethylcyclopentylidene[6] (3) may be considered to be modified tetra-*tert*-butylethylene derivatives where the methyl groups of 1 are "tied back", decreasing the severe steric interactions about the olefinic double bond. A pyrazoline analogue, bi-3,3,5,5-tetramethyl-Δ^1-pyrazolin-4-ylidene[7] (4), could similarly be prepared.

On the basis of these results it appeared reasonable that a useful strategy for the synthesis of tetra-*tert*-butylethylene could involve the preparation of key compounds such as 7 using "twofold extrusion" methods[3,4] (Scheme I). If X were chosen to be an easily extrudable moiety, it could serve to "tie back" the methyl groups of 5, decreasing steric hindrance about the carbonyl groups and allowing the preparation of an intermediate such as 6.[8] Careful choices of Y and Z would keep the bulky substituents as far apart as possible in the intermolecular reaction forming 6 yet would allow for their simple removal in an intramolecular reaction, affording the olefin 7. Reductive removal of X would cleave the cyclic system, liberating the desired *tert*-butyl moieties.

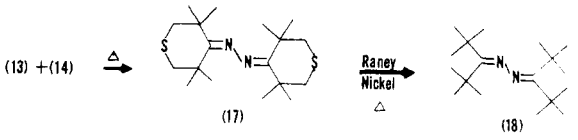
An obvious choice for X would be sulfur; Raney nickel desulfurization could cleave the thiacyclohexane system in 7 without significant reaction at the very sterically hindered double bonds of 7 or 1. An ideal choice for 6 would be a selenadiazoline (Y = Se, Z = N_2).[4] This reactive intermediate could be prepared by reaction of a selone with a diazo compound; thermal extrusion of molecular nitrogen and selenium from 6 would generate the olefinic bond of 7.

The desired thiacyclohexanone 10 could not be obtained by direct alkylation of 4-thiacyclohexanone. It was prepared, however, by a known multistep procedure[8c,9] starting from thiodipivalic acid (9), which in turn could be easily prepared from pivalolactone (8,[10] Scheme II). Ketone

Scheme III



Scheme IV



Scheme V

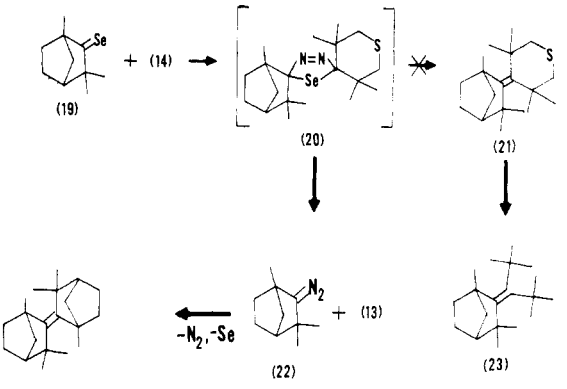
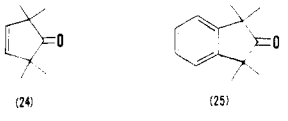


Chart II



10 was cleanly converted in 74% yield to the crystalline hydrazone 11 by heating with hydrazine hydrate in diethylene glycol. Treatment of 11 with triphenylphosphine dibromide and triethylamine afforded the crystalline triphenylphosphoranylhydrazone 12 in 79% yield. Heating 12 under reduced pressure with selenium powder, while continuously distilling volatiles, afforded upon purification the reactive selone 13 as a deep blue liquid in 62% yield.

The utility of 13 as an intermediate in the synthesis of very sterically hindered olefins was demonstrated in the preparation of the known 1,1-diphenyl-2,2-di-*tert*-butylethylene[3] (16). Treatment of 13 at room temperature with diphenyldiazomethane[3] led to spontaneous evolution of nitrogen and rapid extrusion of selenium (Scheme III). Chromatographic purification led to formation of 4-(diphenylmethylene)-3,3,5,5-tetramethylthiacyclohexane (15) in 72% yield. Raney nickel desulfurization converted 15 to the desired olefin 16 in 56% yield. Under these desulfurization conditions 16 is completely stable.

Treatment of the selone 13 under a variety of reaction conditions with the corresponding unstable diazo compound 14 (obtained by pyrolysis of the triphenylphosphoranylhydrazone 12) afforded no olefinic compounds and only small amounts of material which could be characterized as the azine 17 (Scheme IV). Raney nickel desulfurization[11] cleanly afforded the known di-*tert*-butyl ketone azine (18).

An attempt to prepare the less sterically hindered (di-*tert*-butylmethylene)fenchane (23) by using diazo compound 14 gave an apparently anomalous result. Treatment

(2) G. J. Abruscato and T. T. Tidwell, *J. Org. Chem.*, **37**, 4151 (1972).
(3) D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans. 1*, 1794 (1974).
(4) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, 2079 (1976).
(5) G. A. Olah and G. K. Surya Prakash, *J. Org. Chem.*, **42**, 580 (1977).
(6) A. Krebs and W. Rüger, *Tetrahedron Lett.*, 1305 (1979).
(7) R. J. Bushby, M. D. Pollard, and W. S. McDonald, *Tetrahedron Lett.*, 3851, (1978); R. J. Bushby and M. D. Pollard, *J. Chem. Soc., Perkin Trans. 1*, 2401 (1979).
(8) Similar strategies have been used in the syntheses of o-di-*tert*-butyl aromatic compounds: (a) L. R. C. Barclay, C. E. Milligan, and N. D. Hall, *Can. J. Chem.*, **40**, 1664 (1962); (b) A. W. Burgstahler and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **85**, 173 (1963); (c) A. De Groot and H. Wynberg, *J. Org. Chem.*, **31**, 3954 (1966).
(9) A. DeGroot, J. A. Boerma, J. DeValk, and H. Wynberg, *J. Org. Chem.*, **33**, 4025 (1968).
(10) We gratefully acknowledge the assistance of Dr. John Hyatt, Tennessee Eastman Corp., for generously supplying pivalolactone and the procedure for converting this compound to thiodipivalic acid.
(11) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, 1967, p 729.

of 14 with selenofenchone (19) afforded a bifenchylidene mixture as the only olefinic components. It appears that the initially formed selenadiazoline intermediate 20 did not fragment as desired but underwent a retrocyclization affording diazofenchane (22). This would readily react with selenofenchone (19) to form the less sterically hindered selenadiazoline. Normal extrusion pathways would afford the bifenchylidene[12] (Scheme V).

From these results, it appears that the thiacyclohexanone derivatives were only moderately useful in "tying back" *tert*-butyl groups. It is likely that the long carbon–sulfur bonds do not adequately relieve steric strain in the area of the methyl groups. Increased ring strain, as in carbocyclic systems such as 24 or 25 (Chart II) would be necessary to allow significant formation of a selenadiazoline and to allow "normal" fragmentation of this intermediate to form a very sterically hindered double bond. Approaches to the synthesis of tetra-*tert*-butylethylene along these lines are currently underway.

Experimental Section

General Methods. GLC analyses were performed by using a Perkin-Elmer 3920 chromatograph and a stainless-steel column (6 ft × $^1/_8$ in.) filled with 8% OV-17 on Chromosorb W-HP unless otherwise indicated (80–100 mesh, operating at 250 °C, carrier gas nitrogen, flame-ionization detector). ^{1}H NMR spectra were recorded with a Varian EM360L using tetramethylsilane as an internal standard. IR spectra were recorded with a Perkin-Elmer 727B spectrometer. Mass spectra were obtained by using a Hitachi Perkin-Elmer RM U-6L. TLC analyses were performed with Eastman 13181 silica gel. Solvents were evaporated by using a rotary evaporator under reduced pressure. Anhydrous magnesium sulfate was used as a drying agent for compounds in organic solvents.

Thiodipivalic Acid[10] (9). A solution of sodium hydrosulfide was prepared by passing hydrogen sulfide into sodium hydroxide (40 g, 1.0 mol) in 300 mL of water until a weight increase of 34 g was obtained. Pivalolactone[10] (100 g, 1.0 mol) was added slowly with stirring while the temperature of the reaction mixture was maintained at 10–15 °C with external cooling. After this addition, a solution of sodium hydroxide (40 g, 1.0 mol) in 250 mL of water was added while the temperature was kept below 20 °C. Additional pivalolactone (100 g, 1.0 mol) was added dropwise while the temperature was kept at 20–35 °C, and the reaction mixture was then heated to reflux for 2 h. Concentrated hydrochloric acid was added until the mixture was acidic, and the precipitated solid was isolated by filtration and washed several times with water. After being dried, the solid weighed 190 g (81%); mp 162–163 °C (lit.[8c] mp 163–164 °C).

3,3,5,5-Tetramethylthiacyclohexan-4-one Hydrazone (11). 3,3,5,5-Tetramethylthiacyclohexan-4-one[9] (5.0 g, 29 mmol) and hydrazine monohydrate (6.25 mL, 6.44 g) in diethylene glycol (12.5 mL) were heated to reflux for 48 h. The reaction mixture was poured into cold water and extracted with ether (3 × 25 mL). The ethereal solution was washed with water and saturated NaCl solution, dried, and concentrated to give colorless crystals. Recrystallization from hexanes gave the hydrazone (4.0 g, 74%) as colorless plates: mp 107–109.5 °C; IR ($CHCl_3$) ν_{max} 3420, 1640, 1470, 1375, 1270, 1070 cm^{-1}; NMR ($CDCl_3$) δ 4.60 (br s, 2 H), 2.60 (s, 2 H), 2.55 (s, 2 H), 1.42 (s, 6 H), 1.25 (s, 6 H). Anal. Calcd for $C_9H_{18}N_2S$: C, 58.01; H, 9.74; N, 15.03. Found: C, 58.06; H, 9.73; N, 14.90.

3,3,5,5-Tetramethylthiacyclohexan-4-one Triphenylphosphoranylenehydrazone (12). Bromine (1.57 g, 9.8 mmol) in dry benzene (12 mL) was added over 30 min to a stirred, ice-bath-cooled solution of triphenylphosphine (2.58 g, 9.8 mmol) in dry benzene (30 mL). After an additional 30 min of stirring, 11 (1.83 g, 9.8 mmol) and triethylamine (3.0 mL) in dry benzene (10 mL) were added over a period of 1 h. After 5 h at room temperature the mixture was filtered and concentrated to give yellow crystals. Recrystallization from chloroform/hexanes gave the phosphazine (3.44 g, 79%) as three crops of yellow needles: mp 135–136 °C; IR ($CHCl_3$) ν_{max} 1720, 1450, 1370, 1240, 1120 cm^{-1}; NMR ($CDCl_3$) δ 7.55 (m, 15 H), 2.58 (s, 2 H), 2.54 (s, 2 H), 1.73 (s, 6 H), 1.15 (s, 6 H). Anal. Calcd for $C_{27}H_{31}N_2PS$: C, 72.61; H, 6.99; N, 6.27. Found: C, 72.55; H, 6.97; N, 6.18.

3,3,5,5-Tetramethylthiacyclohexane-4-selone (13). Compound 12 (928 mg, 2.1 mmol) and selenium powder (416 mg) were heated in an oil bath at 160 °C for 2 h while volatiles distilled at 1 torr into a dry ice–acetone trap, affording a blue oil which contained the selone, small amounts of diazo compound, and rearrangement products. Bulb to bulb distillation gave pure selone (312 mg, 62%) as an unstable dark blue liquid which solidifies at dry ice temperatures: IR (neat) ν_{max} 1720, 1490, 1400, 1380, 1050, 1020 cm^{-1}; NMR (CCl_4) δ 2.78 (s, 4 H), 1.53 (s, 12 H); exact mass calcd for $C_9H_{16}S^{80}Se$ 236.01380, found 236.01211.

4-Diazo-3,3,5,5-Tetramethylthiacyclohexane (14). Compound 12 (68 mg, 1.5 mmol) was heated to 140 °C, and the diazo compound was continually distilled at 1 torr into a dry ice–acetone trap. Bulb to bulb distillation gave unstable orange crystals at room temperature (100 mg, 0.5 mmol, 33%) which decomposed quickly upon heating: IR (neat) ν_{max} 2050, 1480, 1400, 1380, 1270, 1170, 1120 cm^{-1}; NMR (CCl_4) δ 2.64 (s, 4 H), 1.2 (s, 12 H).

3,3,5,5-Tetramethyl-4-(diphenylmethylene)thiacyclohexane (15). Compound 13 (111 mg, 0.47 mmol) and diphenyldiazomethane[3] (92 mg, 0.47 mmol) in 0.5 mL of tetrahydrofuran were stirred for 16 h at room temperature, and then the mixture was heated to reflux for 19 h. Evaporation of the solvent with a stream of nitrogen and recrystallization from aqueous ethanol gave the pure olefin (110 mg, 72%) as colorless needles: mp 201–202 °C; IR ($CHCl_3$) 1720, 1370, 1240 cm^{-1}; NMR ($CDCl_3$) δ 7.13 (s, 10 H), 2.55 (complex, 4 H), 1.11 (s, 12 H). Anal. Calcd for $C_{22}H_{26}S$: C, 81.93; H, 8.13; S, 9.94. Found: C, 81.99; H, 8.33; S, 9.70.

Raney Nickel Reduction of 15. To 15 (10 mg, 0.31 mmol) was added Raney nickel (from 2.0 g of alloy activated according to Fieser[11]) in ethanol (20 mL). The mixture was heated to reflux for 10 min, filtered through Celite, and concentrated. Analysis by GC (OV-17, DC-710), NMR, and TLC showed unreacted 15 (~25%), 16 (~56%), and a slightly more volatile compound (~19%). Longer reaction times (2 h) led to complete reduction of 15 with no significant change in the relative ratios of the other two components. Fractional kugelrohr distillation afforded olefin 16[3] in 20% isolated yield. 16 is completely stable under these Raney nickel desulfurization conditions.

Attempted Preparation of Bi-3,3,5,5-Tetramethylthiacyclohexylidene (7). Compounds 13 (75 mg, 0.32 mmol) and 14 (63 mg, 0.34 mmol) in dry tetrahydrofuran (0.5 mL) under dry nitrogen were stirred for 3 days, and then the mixture was heated to reflux for 6 days. Distillation of the reaction mixture at 90 °C (0.5 torr) gave a small amount of rearrangement products but no starting materials. Kugelrohr distillation of the residue at 107 °C (0.5 torr) afforded a colorless crystalline film which proved to be 3,3,5,5-tetramethylthiacyclohexan-4-one azine 17 (24 mg, 21%): mp 100–105 °C; IR (CCl_4) ν_{max} 1720, 1600, 1480, 1390, 1370, 1220 cm^{-1}; NMR (CCl_4) δ 2.56 (s, 4 H), 2.50 (s, 4 H), 1.33 (s, 24 H); exact mass calcd for $C_{18}H_{32}N_2S_2$ 340.20070, found 340.19889.

Raney Nickel Reduction of 17. To 17 (5.2 mg, 0.015 mmol) was added Raney nickel (from 4.0 g of alloy activated according to Fieser[11]) in ethanol (25 mL). The mixture was heated to reflux for 10 min, filtered through Celite, and concentrated. Analysis by TLC, GC, and NMR showed a singlet component identical with di-*tert*-butyl azine 18.[4]

Reaction of (−)-1,3,3-Trimethylnorbornane-2-selone (Selenofenchone) (19) with 12 or 14. Compounds 19 (500 mg, 2.3 mmol) and 12 (950 mg, 2.2 mmol) were heated to 155 °C for 24 h at which time NMR showed complete disappearance of 12. Chromatography on silica gel (hexanes) afforded a (−)-1,1′,3,3,3′,3′-hexamethyl-2,2′-binorbonylidene mixture (2; 180 mg, 28%) as the only olefinic products (NMR, GC, TLC). Reaction of 19 with 14 afforded the same product.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank

(12) Similar reactions of very sterically hindered thia- and selenadiazolines have been previously reported.[4,7]

Dr. Paul Vouros of Northeastern University for providing low-resolution mass spectra and Dr. Catherine Costello director of the MIT Mass Spectra Facility, which is operated under the sponsorship of the National Institutes of Health (Grant No. RR00317), for providing high-resolution mass spectra. We also thank Mr. Henry Hsia for his assistance in experimental work.

Registry No. 2, 73745-81-0; 8, 1955-45-9; 9, 73712-47-7; 10, 17539-61-6; 11, 73712-48-8; 12, 73712-49-9; 13, 73712-50-2; 14, 73712-51-3; 15, 73712-52-4; 16, 54396-71-3; 17, 73712-53-5; 18, 61833-36-1; 19, 56956-24-2; sodium hydrosulfide, 16721-80-5; diphenyldiazomethane, 883-40-9.

Stereospecific Palladium-Promoted Oxyamination of Alkenes

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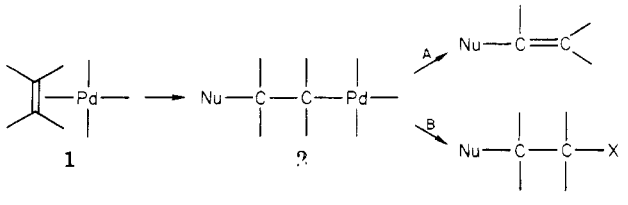
A method for direct oxyamination of olefins to vicinal amino alcohol derivatives is described. The reaction proceeds via an aminopalladation–oxidation sequence. Terminal olefins give good yields (60–80%) whereas internal olefins give lower yields (20–60%). The oxyamination reaction is stereospecific as shown by reaction of (*Z*)- and (*E*)-2-butene and (*E*)-1-deuterio-1-decene and proceeds by overall cis stereochemistry. The stereochemical outcome is a result of a trans aminopalladation followed by an oxidative cleavage of the palladium carbon bond with inversion of configuration at carbon. Oxidation of the organopalladium σ complex to give an oxidized palladium intermediate, which could be a Pd(IV) intermediate, followed by S_N2-type nucleophilic displacement of palladium is the most likely mechanism for the oxidative cleavage reaction.

Organometallic reagents, in particular those of transition metals, have become important tools in organic synthesis, and today a great number of organic transformations utilizing transition metals are known.[1,2] Because of their ability to coordinate and activate alkenes, transition-metal reagents are particularly useful for the functionalization of double bonds. We have recently been concerned with palladium-promoted functionalization of double bonds involving carbon–nitrogen bond formation to give amines, diamines, and amino alcohol derivatives.[3-5]

The general route for palladium-promoted or -catalyzed functionalization of olefins involves π-complex formation (1) followed by nucleophilic attack on the coordinated olefin (Scheme I). In this process the olefin may be attacked either by a coordinated nucleophile (e.g., alkyl) or by a free nucleophile (e.g., amine, acetate, or alcohol). Cleavage of the palladium–carbon bond in the intermediate σ complex **2** may take place in two principal ways: β elimination (A) or substitution of the palladium atom (B). Examples of the first type of reaction (A) include palladium-catalyzed arylation (Nu = Ar)[6] and the vinyl acetate process (Nu = OAc).[7] The Wacker process may also be considered as such a reaction (Nu = OH).[8]

Scheme I



Cleavage of the metal carbon bond according to the second path (B) may, for example, be a reduction (X = H),[5] an insertion (X = COOR),[9] or an oxidative cleavage process (X = OR, R_2N, Cl, Br).[3,4,10]

In a preliminary paper[3] we reported a method for vicinal cis oxyamination of olefins, which in principle takes place as depicted in Scheme I (path B; Nu = NR_2, X = OAc), using palladium in stoichiometric amounts. This procedure also required one equivalent of lead tetraacetate. We have now found that lead tetraacetate can be replaced by other oxidants (e.g., NBS, Br_2, I_2), which in the presence of an oxygen nucleophile (CH_3COO^-, OH^-, ArO^-) readily cleave the palladium–carbon bond in the aminopalladation adduct to give the desired product. In this paper we report these new results and also give full details of the previous report.

Results and Discussion

Olefins were transformed in a "one-pot" reaction to a vicinal amino alcohol derivative (e.g., amino acetate). A β-aminopalladium complex is readily obtained from the corresponding olefin by aminopalladation[5] at −40 °C. The oxidative cleavage of the palladium–carbon bond in such adducts was studied by using different oxidants in the presence of an oxygen nucleophile. Most such cleavage

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