Table II. Comparison of the Terminal Alkene Selectivity from the Dehydration of 2-Butanol and Methyl-Substituted 2-Butanols

alcohol	alumina catalyst	zirconia catalyst
2-butanol	45[a]	90
2-methyl-2-butanol (VII)	50	47
3-methyl-2-butanol (VI)	25	94
2,3-dimethyl-2-butanol (V)	84–89	67

[a] Reference 9.

study. Thus, the alkene distributions represent the primary reaction product distribution that desorbs to the gas phase.

The results clearly show that we cannot account for the alkene selectivity using only steric interactions in the transition state. For the alcohols in Table II the selectivity does not change according to the number of β-hydrogens for either alumina or zirconia. With zirconia it appears that the substituent at the internal β-H position has little effect on the alkene selectivity, but that substitution at the α-H position does change the selectivity to favor more Saytzeff product. Substitution at either the 2- or 3-position influences the alkene selectivity obtained with alumina. It appears that in addition to steric effects in the transition state, the geometry of the catalytic site and electronic factors may play a role in determining the alkene selectivity of heterogeneous catalysts.

Experimental Section

Zirconia was prepared by rapidly adding a 3–5-fold excess of concentrated ammonium hydroxide to a 1 M zirconium nitrate solution.[8] The precipitate was washed with distilled water to peptization, dried at 120 °C, and calcined in air at 600 °C. Alumina was prepared by the hydrolysis of aluminum isopropoxide (dissolved in 2-propanol) with water. Washing with distilled water was followed by drying at 120 °C. The B.E.T. surface area for zirconia was 40 m^2/g; alumina was about 200 m^2/g.

The catalyst, held in a plug flow reactor below a glass bead preheater section, was heated in situ in hydrogen at 500 °C. The catalyst was then cooled to reaction temperature in hydrogen. The reactant was pumped over the catalyst, using a syringe pump, without diluent. Liquid samples were collected at intervals and analyzed by GC (Carbowax 20M programed at 15 °C/min from 40 °C for conversion, OV-1 operated isothermally for alkene distribution).

Alcohols were dehydrated by sulfuric acid (1 or 10 wt %) in acetic acid at 25 °C.[3] Aliquots were removed at intervals and quenched in water. Unconverted alcohol and alkenes products were extracted into mesitylene prior to analysis by GC.

Registry No. 2-Butanol, 78-92-2; 2-methyl-2-butanol, 75-85-4; 3-methyl-2-butanol, 598-75-4; 2,3-dimethyl-2-butanol, 594-60-5.

Communications

Bis(trimethylsilyl) Peroxide for the Baeyer–Villiger Type Oxidation[1]

Summary: A Baeyer–Villiger type oxidation of ketonic substrates is achievable under aprotic conditions by use of bis(trimethylsilyl) peroxide and a catalytic amount of trimethylsilyl trifluoromethanesulfonate. The oxidation occurs specifically at carbonyl function and carbon–carbon double bonds are not affected.

Sir: Readily accessible bis(trimethylsilyl) peroxide (1)[2] is viewed as a masked form of 100% hydrogen peroxide. This unique peroxide, unlike hydrogen peroxide, possesses reasonable thermal stability and high solubility in ordinary aprotic organic solvents, and hence can be easily handled. In addition, the silyl group endows the oxygen atoms attached to it with eminent nucleophilicity with respect to oxygens in parent hydrogen peroxide.[3] Despite such characteristic features, however, its synthetic application has been quite lmited.[4] We have found that the bis(silyl) peroxide, when combined with trimethylsilyl trifluoromethanesulfonate (2) as catalyst,[5] is useful for the Baeyer–Villiger type reaction of a range of ketones (eq 1).[6,7]

$$R_2C{=}O + (CH_3)_3SiOOSi(CH_3)_3 \xrightarrow[-[(CH_3)_3Si]_2O]{\text{cat. }(CH_3)_3SiOTf\ (\mathbf{2})} RCOOR \quad (1)$$

The reaction was conducted in dichloromethane by using an equimolar mixture of a ketone and the peroxide 1 with

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[1] Trialkylsilyl Triflates in Organic Synthesis. 13. Part 12: Murata, S.; Suzuki, M.; Noyori, R. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 247.

[2] Ham, W.; Metzinger, L. *Makromol. Chem.* **1956**, *21*, 113. Dannley, R. L.; Jalics, G. *J. Org. Chem.* **1965**, *30*, 2417. Tarabarina, A. P.; Jablokov, V. A.; Jablokova, N. V. *Z. Obsch. Chim.* **1970**, *40*, 1094. For practical synthesis of 1, see: Cookson, P. G.; Davies, A. G.; Fazal, N. *J. Organometal. Chem.* **1975**, *99*, C31.

[3] Oberhammer, H.; Boggs, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7241, and references cited therein.

[4] Reactions were examined only with pyridine, sulfides, thiols, disilanes, Grignard reagents, alkyllithiums, $Ni(CO)_4$, sodium ethoxide, lead tetraacetate, alkali metals, CrO_3, SO_2, SO_3, HCl, etc. See: Blaschette, A.; Bressel, B.; Wannagat, U. *Angew. Chem.* **1969**, *81*, 430. Bressel, B.; Blaschette, A. *Z. Anorg. Allg. Chem.* **1970**, *377*, 182. Brandes, D.; Blaschette, A. *J. Organometal. Chem.* **1973**, *49*, C6. Tamao, K.; Kumada, M.; Ishikawa, M. *Ibid.* **1971**, *31*, 17. Tamao, K.; Kumada, M. *Ibid.* **1971**, *31*, 35.

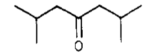
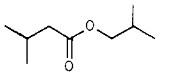
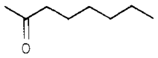
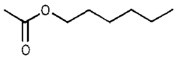
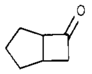
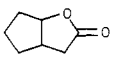
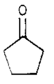
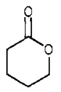
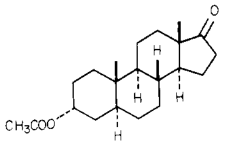
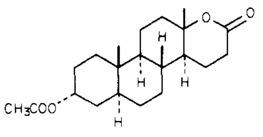
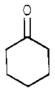
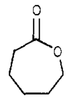
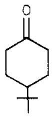
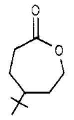
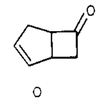
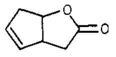
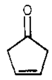
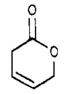
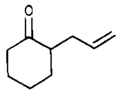
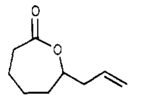
[5] For synthetic utility of trimethylsilyl triflate, see: Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* (Tetrahedron Symposium in Print, Corey, E. J., Ed.) **1981**, *37*, 3899.

[6] For reviews on the Baeyer–Villiger oxidation, see: Hassall, C. H. *Org. React.* **1957**, *9*, 73. House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin; Menlo Park, CA, 1972; pp 321–329. Lewis, S. N. In "Oxidation"; Augustine, R. L., Ed.; Marcel Dekker: New York, 1969; Vol. 1, p 213.

[7] For oxidation of ketones with hydrogen peroxide, see: (a) With added BF_3 catalyst; McClure, J. D.; Williams, P. H. *J. Org. Chem.* **1962**, *27*, 24. (b) In aqueous acetic acid; Corey, E. J.; Arnold, Z.; Hutton, J. *Tetrahedron Lett.* **1970**, 307. (c) With hexafluoroacetone; Chambers, R. D.; Clark, M. *Tetrahedron Lett.* **1970**, 2741. (d) With arsonated polystyrene; Jacobson, S. E.; Mares, F.; Zambri, P. M. *J. Am. Chem. Soc.* **1979**, *101*, 6938. (e) With acetonitrile; Gibson, D. H.; Joseph, J. T. *Tetrahedron Lett.* **1972**, 3483.

0022-3263/82/1947-0902$01.25/0

Table I. Baeyer-Villiger Type Oxidation of Ketones[a]

entry	ketone	conditions: TMSOTf, mol %	conditions: temp, °C (time, h)	product (% yield[b])
1		10	0 (22)	 (40)
2		10	−78 to −30 (33)	 (24)
3		10	−40 to −35 (4.5)	 (73)
4		3.5	−78 (1) and −30 to −20 (8)	 (58)[c]
5		11	−25 to −10 (20)	 (70,[d] 86[e])
6		5	−78 (6) and −40 (1)	 (76)[c]
7		10	−25 to 0 (5)[f]	 (57)
8		10	−40 to −35 (4.5)	 (75)
9		10	−78 to −50 (30) and 0 (20)	 (42)
10		16	−78 (3) and −50 to −10 (4.5)	 (40)[d]

[a] Unless otherwise stated, the reaction was carried out in dichloromethane. All compounds were identified by comparison of the chromatographic and/or spectral properties with those of authentic samples. [b] Determined by ^{1}H NMR analysis. [c] GLC yield. [d] Isolated yield. [e] Based on consumed starting material. [f] Reaction in a 1:2 mixture of dichloromethane and nitromethane.

a small amount of 2. The oxidation proceeds under aprotic conditions and below 0 °C. Several examples are given in Table I. This method is applicable to a variety of ketonic substrates, particularly cyclic ketones.[8] Notably, this oxidation occurs specifically at carbonyl function and carbon–carbon double bonds are left intact. Thus when a 1:1 mixture of cyclohexanone and cyclohexene was treated with 1 and 2 under the standard conditions, 6-hexanolide was obtained but no trace of cyclohexene oxide was detected. The intramolecular competition of the functional groups is exemplified by the experiments of entries 8–10. Bicyclo[3.2.0]hept-2-en-6-one upon exposure to 1 with added 2 led exclusively to a prostaglandin intermediate (entry 8).[9] The oxidation of 3-cyclopentenone afforded solely 3-penten-5-olide (entry 9). This lies in sharp contrast to the oxidation by trifluoroperacetic acid which produces only 3,4-epoxycyclopentanone.[10,11] The reaction of 2-allylcyclohexanone took place in a chemo- and regioselective manner to give 6-allyl-6-hexanolide as a sole product (entry 10). The major byproducts, as examined with cyclohexanone as substrate, were the dimeric and trimeric cyclic peroxides.[12] It should be added that aromatic ketones are not employable; attempted oxidation of various alkyl phenyl ketones resulted in the formation of deteriorated reaction mixtures.

The oxidation catalyzed by 2[13] is considered to proceed

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[8] Oxidation of cyclohexanone with H_2O_2/hexafluoroacetone was reported to give 6-hexanolide in 50% yield.[7c]

[9] Corey, E. J.; Noyori, R. *Tetrahedron Lett.* **1970**, 311.

[10] Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623.

[11] Oxidation with *m*-chloroperbenzoic acid (CH_2Cl_2, 20 °C, 48 h) gave the epoxide and unsaturated lactone in 63% and 6% yield, respectively.

[12] Criegee, R.; Schnorrenberg, W.; Becke, J. *Justus Liebigs Ann. Chem.* **1949**, *565*, 7. Story, P. R.; Lee, B.; Bishop, C. E.; Denson, D. D.; Busch, P. *J. Org. Chem.* **1970**, *35*, 3059 and references cited therein.

[13] Activating agents other than 2 could be used but much less effectively. For example, percent yields of 6-hexanolide in the oxidation of cyclohexanone and 1 in CH_2Cl_2 were as follows: $AlCl_3$ 30 (100 mol %, 0 °C/4 h and 25 °C/3 h), 6 (10 mol %, 0 °C/4 h and 25 °C/18 h); $TiCl_4$ 19 (130 mol %, 0 °C/3 h and 25 °C/5 h), 14 (23 mol %, 0 °C/3 h and 25 °C/5 h); BF_3 70 (110 mol %, −70 to −50 °C/22 h), 3 (6 mol %, −78 to −70 °C/21 h); $(CH_3)_3SiI$ 4 (10 mol %, 0 °C/18 h and 25 °C/3 h), 12 (10 mol %, −78 to −70 °C/21 h). Recently, Professor H. Nozaki of Kyoto University informed us that $SnCl_4$ is an effective stoichiometric promoter.

by the mechanism outlined in eq 2–5. High stability of hexamethylsiloxane would be the driving force of the fragmentation of the initially formed tetrahedral intermediate 4.[14]

$$R_2C{=}O + 2 \rightleftharpoons \underset{3}{R_2C{=}O^+{-}Si(CH_3)_3TfO^-} \tag{2}$$

$$3 + 1 \rightarrow \underset{4}{R_2C[OSi(CH_3)_3]OOSi(CH_3)_3} + 2 \tag{3}$$

$$4 + 2 \rightleftharpoons \underset{5}{R_2C[OSi(CH_3)_3]OO^+[Si(CH_3)_3]_2TfO^-} \tag{4}$$

$$5 \rightarrow RCOOR + [(CH_3)_3Si]_2O + 2 \tag{5}$$

The following procedure is representative (entry 5). A dichloromethane[15] solution (7 mL) of the triflate 2 (44 mg, 0.20 mmol) was placed in a dried glass vessel under argon atmosphere and cooled to −40 °C. To this were successively added under stirring the bis(silyl) peroxide 1 (412 mg, 2.2 mmol, 96% pure) and a cooled (−40 °C) solution of androsterone acetate (633 mg, 1.9 mmol) in dichloromethane[15] (2 mL). The resulting mixture was warmed to −25 °C and stirred at −25 to −10 °C for 20 h, then poured into an ice-cooled, saturated $NaHCO_3$ aqueous solution (30 mL), and extracted with ether (40 mL × 2).[16] The combined ethereal extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residual material was chromatographed on silica gel (20 g) by using a 5:1:1 mixture of hexane, ethyl acetate, and benzene as eluant to give recovered starting material (117 mg, 19%) and the corresponding lactonic product (461 mg, 70% yield or 86% yield based on the consumed ketone), mp 184–186 °C.

Registry No. 1, 5796-98-5; 2,6-dimethyl-4-heptanone, 108-83-8; 2-octanone, 111-13-7; bicyclo[3.2.0]heptan-6-one, 13756-54-2; cyclopentanone, 120-92-3; 3-(acetyloxy)androstan-17-one, 1164-95-0; cyclohexanone, 108-94-1; 4-(1,1-dimethylethyl)cyclohexanone, 98-53-3; bicyclo[3.2.0]hept-2-en-6-one, 13173-09-6; 3-cyclopenten-1-one, 14320-37-7; 2-(2-propenyl)cyclohexanone, 94-66-6; 2-methylpropyl 3-methylbutanoate, 589-59-3; hexyl acetate, 142-92-7; hexahydro-2*H*-cyclopenta[*b*]furan-2-one, 5745-61-9; tetrahydro-2*H*-pyran-2-one, 542-28-9; 3-(acetyloxy)-*D*-homo-17a-oxaandrostan-17-one, 80629-95-4; 2-oxepanone, 502-44-3; 5-(1,1-dimethylethyl)-2-oxepanone, 34680-83-6; 3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*b*]furan-2-one, 34638-25-0; 3,6-dihydro-2*H*-pyran-2-one, 26677-08-7; 7-(2-propenyl)-2-oxepanone, 68854-26-2.

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[14] Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357.

[15] Freshly distilled from P_2O_5.

[16] In this particular reaction, potassium iodide test was negative at this stage. When some peroxides remain, the mixture should be subjected to appropriate reductive workup to destroy them.