

Reduction of Colorflamme. Four milligrams of colorflamme was dissolved in 2.5 mL of ethanol and 0.5 mL of H₂O, and the mixture was stirred for 2 h with addition of 10 mg of NaBH₄. The alcohol was evaporated by blowing N₂ over the solution, and then the residue was extracted 3 times with ether. The ether was dried with anhydrous Na₂SO₄ and evaporated under reduced pressure. A white amorphous residue remained (trihydro derivative). This was repeated with NaBD₄, C₂H₅OD, and D₂O (trideuterio derivative).

Trihydro Derivative. The trihydro derivative had the same *R_f* values in systems S3-S6 as limacine. The other possible diastereoisomer (homoaromoline) could not be observed on TLC in the reaction product. UV λ_{\max} 281 nm; mass spectrum, (230 °C), *m/e* 609 (6.3), 608 (M⁺, 16.8), 607 (8.4), 501 (0.5), 381 (8.9), 228 (15.8), 198 (8.4), 193 (21), 192 (100), 191.5 (6.3), 191 (36.8), 190 (31.6); exact mass calcd for C₃₇H₄₀N₂O₆ 608.2894, found 608.2884; ¹H NMR (250 MHz) δ 2.50 (dd, H_{2,2}), 2.50-2.90 (m, 5 H), 2.55 (s, NCH₃), 2.57 (s, N'CH₃), 2.82 (dd, H_{2,2}), 2.90-3.06 (m, 2 H), 3.12 (d, H_{1,1}), 3.40 (d, H_{1,1}), 3.42 (s, 6-OCH₃), 3.59 (d, H₁), 3.45-3.52 (m, 1 H), 3.78 (s, 6'-OCH₃), 3.95 (s, 12-OCH₃), 4.36 (d, H'₁), 5.2-5.4 (br s, OH), 6.38 s, H₅), 6.41 (s, H₈), 6.45 (s, H₆), 6.57 (s, H₁₀), 6.83 (br s, H₁₃' and H₁₄'), 6.92 (d, H₁₄), 6.96 (d, H₁₃), 7.10 (d, H₁₂), 7.36 (d, H₁₁). **Note:** The shifts and coupling constants of the various protons (an exception are the methoxy protons) are extremely sensitive to temperature changes and traces of acid or base, even in CDCl₃. Shift variations of 0.15 ppm for some protons under apparently the same conditions were observed. Future workers who want to compare their data with the ones presented here should bear this in mind. ¹³C NMR (only aliphatic carbons; 63 MHz) δ 22.6, 26.4, 40.1, 41.1, 42.2, 43.2, 44.2, 46.5, 55.5, 56.1, 56.4, 60.6, 65.4; optical rotation [α]_D²⁰ +70° (*c* 0.03).

Trideuterio Derivative. UV spectrum and TLC behavior were the same as for the trihydro derivative. Mass spectrum (230 °C), *m/e* (relative intensity) 611 (18), 610 (9), 504 (0.6), 384 (12), 228 (12), 207 (56), 194 (13), 193 (52), 192.5 (20), 191 (18), 190 (15); exact mass calcd for C₃₇H₃₇D₃N₂O₆ 611.3074, found 611.3074; ¹H NMR (250 MHz), similar to that of the trihydro derivative except that the proton at 4.36 ppm and two protons from the multiplet between 2.50 and 2.90 ppm have vanished and that the doublet of doublets at 2.82 ppm has become a doublet; ¹³C NMR (63 MHz), similar to that of the trihydro derivative except for the signals at 22.6, 44.2, and 60.6 ppm, which have vanished.

Limacine. UV, ¹H NMR, and mass spectra were the same as for the trihydro derivative.

Berbacolorflamme: TLC, *R_f* in S₂ 0.44; strong reaction with iodoplatinate reagent, extinction in UV 254 nm, and orange fluorescence in UV 366 nm; UV (MeOH) λ_{\max} 445 nm, 338, 294, 234; UV (MeOH + HCl) λ_{\max} 372 nm, 323, 275, 268, 228; FD mass spectrum, *m/e* 605; ¹H NMR (100 MHz) δ 2.57 (s, 3 H), 3.53 (s, 3 H), 3.85 (s, 3 H), 3.90 (s, 6 H), 4.08 (br s, 1 H), 5.65 (s, 1 H), 6.10-7.52 (aromatic); ¹³C NMR (25.2 MHz) δ 25.6 (t, C₄), 35.4 (t), 35.8 (t), 42.3 (q, NMe), 45.6 (t, C₃), 46.2 (q, NMe), 55.9 (q, OCH₃), 56.2 (q, OCH₃), 56.2 (q, OCH₃), 63.9 (d, C₁), 100.8 (d), 112.1 (d), 112.2 (d), 119.4 (d), 119.4 (s), 121.4 (d), 121.5 (d), 123.0 (s), 123.1 (d), 127.0 (s), 127.4 (s), 128.3 (s), 129.7 (d), 129.8 (s), 132.0 (d), 135.0 (s), 138.5 (s), 143.4 (s), 148.3 (s), 148.6 (s), 149.0 (s), 150.0 (s), 155.5 (s), 162.5 (s); optical rotation [α]_D²⁰ 1000° (*c* 0.004). Reduction of berbacolorflamme was carried out in the same way as described for colorflamme.

Trihydro Derivative. The trihydro derivative had the same *R_f* values in systems S₃-S₆ as limacine. The other possible diastereoisomer (thalrugosine) could not be observed on TLC in the reaction product. UV λ_{\max} 284 nm; mass spectrum (220 °C), *m/e* (relative intensity) 609 (18), 608 (M⁺, 45), 607 (23), 593 (4), 471 (0.5), 381 (27), 367 (9), 198 (8), 193 (18), 192 (100), 191.5 (18), 191 (95), 190 (77); exact mass calcd for C₃₇H₄₀N₂O₆ 608.2870, found 608.2886; ¹H NMR δ 2.36 (s, NCH₃), 2.66 (s, N'CH₃), 3.37 (s, 6'-OCH₃), 3.78 (s, 6-OCH₃), 3.93 (s, 12-OCH₃), 6.05-7.32 (m, aromatic); optical rotation [α]_D²⁰ -205° (*c* 0.008).

Trideuterio Derivative. TLC, the trideuterio derivative had the same *R_f* values in systems S₃-S₆ as limacine; mass spectrum (230 °C), *m/e* (relative intensity) 612 (8), 611 (M⁺, 16), 610 (6), 596 (1.5), 474 (0.1), 384 (13), 370 (3), 198 (11), 193 (52), 192.5 (22), 192 (100), 191 (27), 190 (26).

Limacine (aliphatic carbons only): UV, ¹H NMR, and mass spectra were the same as for the trihydro derivative; ¹³C NMR

(25.2 MHz) δ 21.8 (C-4), 25.6 (C-4'), 37.9 (C- α'), 42.0 (C- α), 42.3 (NMe), 42.7 (NMe'), 44.2 (C-3), 45.4 (C-3'), 56.1 (OCH₃), 56.1 (OCH₃), 56.2 (OCH₃), 61.4 (C-1), 63.8 (C-1').

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Catalytic Conversion of Alcohols. Origin of Anti-Saytzeff Dehydration¹

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Recently Floris reported what was believed to be the first example of an anti-Saytzeff orientation (1-alkene formation from 2-alkanols) for the dehydration of an alcohol with an alumina catalyst.^{2a} Chen and Eloffson^{2b} attributed the selectivity observed by Floris to the stereochemical effect due to hydrogen bonding of the hydroxyl hydrogen to the iron atom of the ferrocenyl group of the 2-ferrocenyl-3-methyl-2-butanol (II) rather than a specific catalytic effect. However, Kieboom³ pointed out that anti-Saytzeff orientation is generally observed in acid-catalyzed dehydration of substituted 2-phenyl-3-methyl-2-butanols (III); presumably steric repulsion in the transition state resulting from interaction of the 3-methyl group with the 2-hydrogen atom of the benzene ring is responsible for the unusual alkene distribution.^{3,4} Kieboom predicted that the isomeric tertiary alcohols CCR-(OH)C(C)C (I) would show anti-Saytzeff orientation for any bulky R substituent.

Pines had reported, prior to Floris' publication, an anti-Saytzeff preference for the dehydration of 2,3-dimethyl-2-butanol (V) with alumina;⁵ we have confirmed the anti-Saytzeff nature of this elimination. We also obtained similar results for the dehydration of 2,3-dimethyl-2-pentanol (IV) with alumina. Thus, with an alumina catalyst, R = methyl is as effective as R = ferrocenyl in promoting formation of the anti-Saytzeff product.

The anti-Saytzeff product predominates (80-91%, Table I) in the dehydration of 2-aryl-3-methyl-2-butanols (III), using a sulfuric acid catalyst in acetic acid solvent. However, when we used Kieboom's procedure to dehydrate V at room temperature with the sulfuric acid in acetic acid, an equilibrium alkene mixture containing only about 10% of the terminal alkene was obtained. This was the result, even at very low conversions. Thus, with 10% sulfuric acid

(1) Based on experimental work done at Potomac State College, Keyser, WV.

(2) (a) Floris, B. *J. Org. Chem.* 1976, 41, 2774. (b) Chen, S. C.; Eloffson, R. M. *Chem. Ind.* 1978, 64.

(3) Kieboom, A. P. G.; Van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* 1969, 88, 1424.

(4) Kieboom, A. P. G. *Chem. Ind.* 1978, 434.

(5) Pines, H.; Manassen, J. *Adv. Catal.* 1966, 16, 49.

Table I. Terminal Alkene Formation from the Conversion of Alcohols

reaction	yield and conditions
$\begin{array}{c} \text{Fe} \quad \text{C} \\ \quad \\ \text{C}-\text{C}-\text{C} \\ \\ \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{Fe} \quad \text{C} \\ \quad \\ \text{C}=\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	92%, Al ₂ O ₃ , 105–100 °C, ref 2a
II Fe = ferrocenyl $\begin{array}{c} \text{R} \quad \text{C} \\ \quad \\ \text{C}-\text{C}-\text{C} \\ \\ \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{R} \quad \text{C} \\ \quad \\ \text{C}=\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	80–91%, H ₂ SO ₄ , 25 °C, ref 4
III R = PhR ₁ $\begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}=\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	92%, Al ₂ O ₃ , 275 °C, ref 5 86%, Al ₂ O ₃ , 220 °C, this work 66%, ZrO ₂ , 220 °C, this work
IV $\begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}-\text{C}-\text{C} \\ \\ \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}=\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	89%, Al ₂ O ₃ , 345 °C; 87% Al ₂ O ₃ , 275 °C, ref 5 84%, Al ₂ O ₃ , 220 °C, this work 67%, ZrO ₂ , 220 °C, this work 10%, H ₂ SO ₄ , 25 °C, this work
V $\begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}-\text{C}-\text{C} \\ \\ \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}=\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	

in solution the 2-phenyl, but not the 2-methyl, group on alcohols of type I provides sufficient steric hindrance to favor the terminal alkene.

Thoria is frequently used as a catalyst with a high selectivity for anti-Saytzeff alkene formation from unsubstituted 2-ols.⁶ However, Lundeen and Van Hoozen,⁷ the first to report this unusual selectivity for thoria, found several transuranium metal oxides had a similar selectivity. We found that zirconia has a selectivity that is similar to that of thoria.⁸

Results obtained from use of a zirconia catalyst demonstrate that the catalyst must play a role in the anti-Saytzeff selectivity obtained with alumina. Zirconia produced 94% of the anti-Saytzeff product from 3-methyl-2-butanol (VI), while only 25% of the terminal alkene was obtained from the dehydration of this alcohol with alumina. Zirconia produced only 67% of the terminal alkene from the tertiary alcohol (V). Thus, zirconia produced greater than 90% of the anti-Saytzeff product from the secondary alcohol (VI) but only 67% of the anti-Saytzeff alkene from an alcohol with structure (I). Alumina showed just the opposite selectivity, producing 84% of the anti-Saytzeff product from the tertiary alcohol (V) but only 25% of the anti-Saytzeff product from the secondary alcohol (VI). With 2-methyl-2-butanol (VII) at 220 °C, both alumina and zirconia produced the same amount of the terminal alkene.

Dehydration of 2-butanol over alumina produced 45% of the terminal alkene and 50% of *cis*-2-butene, while zirconia produced greater than 90% of the anti-Saytzeff alkene (Table II). Replacing the carbinyl hydrogen with a methyl group alters the selectivity so each catalyst

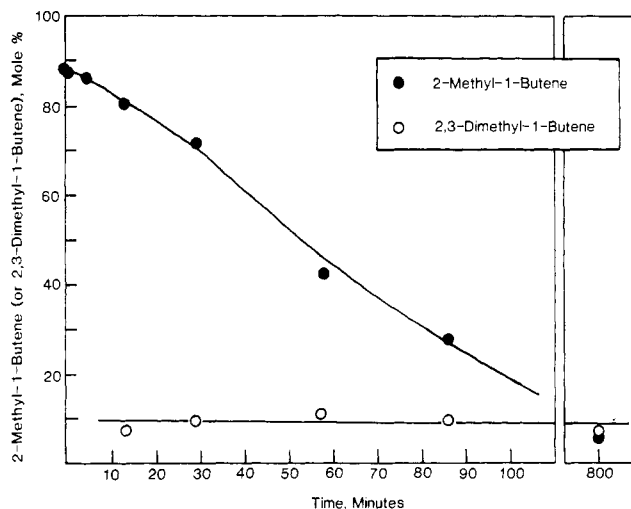


Figure 1. Terminal alkene formed from the conversion of a mixture of 2-methyl-1-butene (10 wt %) and 2,3-dimethyl-2-butanol with 1% H₂SO₄ in acetic acid at 25 °C: (●) 2-methyl-1-butene, (○) 2,3-dimethyl-1-butene.

yielded the same alkene products. A 3-methyl substituent barely alters the alkene selectivity when zirconia catalyzes the dehydration but causes alumina to produce more Saytzeff product. Replacing hydrogens by methyls at both the 2- and 3-positions of 2-butanol causes alumina to produce more anti-Saytzeff product and zirconia to produce less.

Homogeneous and heterogeneous catalysis are similar in some respects. For example, cage effects in homogeneous solution catalysis may trap the initial product long enough for secondary reactions to occur. Likewise, in heterogeneous catalysis desorption may be slow enough to permit secondary reactions to occur prior to desorption to the gas phase. For the above two cases, it is very difficult to identify primary and secondary products. However, when diffusion or desorption from the reaction site is fast compared to that from the secondary reactions, the addition of a similar product enables one to evaluate the extent of secondary reactions.¹⁰

In the present study 2-methyl-1-butene was added to the alcohol reactant (VI or VII) prior to dehydration at 25 °C, using the Kieboom method.³ Similar results were obtained for the dehydration of 2,3-dimethyl-2-butanol (Figure 1) and 2-methyl-2-butanol. If (a) initially 2,3-dimethyl-1-butene was formed selectively as with II and (b) cage effects can be ignored, then the 2,3-dimethyl-1-butene would become a part of the total alkene mixture (methyl- and dimethylbutenes). As such, 2,3-dimethyl-1-butene should isomerize at approximately the same rate as 2-methyl-1-butene. Since the equilibrium dimethylbutene composition was obtained even at short reaction times, 2,3-dimethyl-1-butene was not selectively formed as a dehydration product that escaped from the reaction cage.

Since the Saytzeff orientation is greatly favored by alkene stability for the 2-butanol used in this study,¹¹ the observed anti-Saytzeff alkene selectivity must result from kinetic control. In addition, we have shown that at low alcohol conversion and 1-atm alcohol partial pressure, alkenes added to the alcohol reactant do not undergo significant isomerization with alumina and zirconia catalysts operating in the temperature ranges used in this

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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 m²/g; alumina was about 200 m²/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.

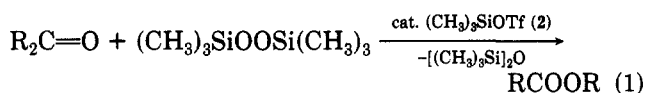
Communications

Bis(trimethylsilyl) Peroxide for the Baeyer-Villiger Type Oxidation¹

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 limited.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}



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

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