32.26, 111.64, 122.25, 125.47, 134.35, 144.66, 145.05; UV λ_{max} 283 nm (log ϵ 4.20).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1056.

2-Isopropenylcyclohepta-1,3-diene (8): retention time 50 min; ^{1}H NMR δ 1.93 (s, 3 H), 1.75–2.65 (m, 6 H), 4.75–5.10 (m, 2 H), 5.98–6.42 (m, 3 H); ^{13}C NMR δ 21.11, 28.09, 28.92, 32.58, 111.54, 127.85, 130.00, 133.75, 139.77, 144.40; UV λ_{max} 247 nm (log ϵ 3.94).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1094.

Synthesis of 7-Isopropenylcyclohepta-1,3,5-triene.[4] Isopropenyllithium was prepared by the dropwise addition of 4.5 mL (0.05 mol) of 2-bromopropene to a stirred suspension of 0.7 g (0.1 mol) of oil-free lithium dust (containing 2% sodium) in 60 mL of dry ether at 0 °C under nitrogen. After the mixture was stirred for 2 h, excess lithium was allowed to float to the top of the solution, which was transferred through a cannula, using positive nitrogen pressure, from the bottom of the flask to an addition funnel. This solution of isopropenyllithium was added dropwise to a rapidly stirred suspension of 8.5 g (48 mmol) of finely ground tropylium fluoroborate in 100 mL of dry ether at 0 °C. The reaction mixture was stirred vigorously for 4 h under nitrogen at 0 °C and then poured into water. The organic layer was separated, washed with 5% HCl, and dried over sodium sulfate. Evaporation under reduced pressure and elution with pentane through a short column of alumina yielded 5.0 g (79%) of the desired product: ^{1}H NMR δ 1.87 (s, 3 H), 2.17 (t, 1 H, J = 5 Hz), 4.92 (s, 2 H), 5.10–5.47 (d of d, 2 H, J = 5 and 9 Hz), 6.00–6.37 (m, 2 H), 6.53–6.73 (t, 2 H, J = 3 Hz).

Exact mass: Calcd for $C_{10}H_{12}$, 132.0939. Found, 132.0862.

Synthesis of 5- and 6-Isopropenylcyclohepta-1,6-dienes (6 and 5). Lithium metal (80 mg, 11.5 mmol) was cut into small pieces and added to a solution of 7-isopropenylcyclohepta-1,3,5-triene (1.0 g, 7.6 mmol) in 100 mL of dry, distilled ammonia at −78 °C. The solution initially turned red and then purple. After the solution was stirred for 1 h, the ammonia was allowed to evaporate at room temperature, and the volatile products were distilled under vacuum into a trap at −78 °C. Preparative GLC on the Carbowax column allowed the separation of **5** and **6**, which were identified by their spectra. The data for **5** were the following: ^{1}H NMR δ 1.60–1.87 (br s, 3 H), 2.43 (s, 5 H), 4.60–4.83 (br s, 2 H), 6.87 (s, 4 H); ^{13}C NMR δ 20.45, 36.76, 44.85, 108.82, 125.48, 132.17, 150.19; UV λ_{max} 253 nm (log ϵ 3.95).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1112.

The spectral data obtained for **6** were the following: ^{1}H NMR δ 1.75 (s, 3 H), 1.50–2.00 (m, 2 H), 2.00–2.50 (m, 2 H), 2.87–3.25 (m, 1 H), 4.63 (s, 1 H), 4.82 (s, 1 H), 5.78 (s, 4 H); ^{13}C NMR δ 20.80, 28.95, 30.14, 49.65, 111.81, 125.12, 132.22, 134.32, 135.99, 148.48; UV λ_{max} 248–9 nm (log ϵ 3.94).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1094.

Acknowledgment. We thank the National Science Foundation and the Alfred P. Sloan Foundation for support of this work.

Registry No. **1**, 62235-10-3; **2**, 72269-00-2; **3**, 57354-42-4; **4**, 72269-01-3; **5**, 72269-02-4; **6**, 72269-03-5; **7**, 72269-04-6; **8**, 72269-05-7; 7-isopropenylcyclohepta-1,3,5-triene, 72269-06-8; tropylium fluoroborate, 27081-10-3; 2-bromopropane, 75-26-3.

Sodium Bismuthate Oxidation of Olefins

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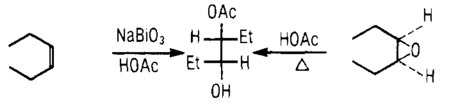
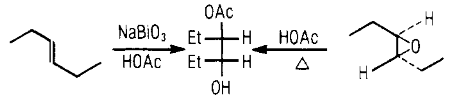
In 1950 Rigby first discovered the synthetic potential of sodium bismuthate in organic oxidations when he demonstrated the cleavage of vicinal diols and the conversion of acyloins to α-diketones in high yield.[2] In spite of Rigby's work and more recent studies by a number of groups on the oxidation of phenols[3-5] with sodium bismuthate, bismuth reagents are seldom used in organic synthesis. Considering the high oxidation potential of bismuth(V) compounds,[6] we decided to explore the oxidation of olefins with sodium bismuthate.[7]

We have found that sodium bismuthate in acetic acid oxidizes olefins to vicinal hydroxy acetates in moderate to low yield (Table I). The yields are highest when a tertiary center is present in the olefin as in trisubstituted and geminally disubstituted olefins. Mono- and 1,2-disubstituted olefins react sluggishly and only afford low yields of hydroxy acetates.[8] The reactions were typically run by mixing equimolar amounts of sodium bismuthate and olefin in glacial acetic acid and stirring the heterogenous mixture in a stoppered flask until the orange color of the sodium bismuthate had dissipated. Filtration and extractive workup afforded the crude products which were further purified by chromatography or distillation to obtain a yield. Under these conditions between half and one-third of the starting olefin was usually recovered. However, the addition of more than 1 molar equiv of oxidant does not improve the yields since the products are unstable to the reaction conditions.

In order to determine whether the olefin maintained its integrity during its exposure to the sodium bismuthate, we examined the three products of oxidation of α-trideuteriomethylstyrene by both GC/MS and NMR. Deuterium scrambling was not observed in either of the products or in the recovered starting material. Furthermore, the olefins react specifically since both (E)-3-hexene and (Z)-3-hexene are converted cleanly to distinguishable hydroxy acetates. The hydroxy acetate obtained from (Z)-3-hexene is identical with that obtained from opening the cis epoxide of 3-hexene and has thus been assigned the threo structure. (E)-3-Hexene similarly affords the erythro hydroxy acetate. The unreacted olefin recovered from these oxidations maintained its stereochemical integrity.





Two mechanistic pathways seemed possible for the production of the hydroxy acetates. They could be generated either by a sodium bismuthate mediated epoxidation of the olefin[9] followed by solvolysis in the acetic acid or via an oxymetalation sequence.[10] To distinguish

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(2) W. Rigby, *J. Chem. Soc.*, 793–5 (1951); 1907–13 (1950).

(3) F. R. Hewgill, B. R. Kennedy, and D. Kilpin, *J. Chem. Soc.*, 2904–14 (1965); F. R. Hewgill and B. S. Middleton, *J. Chem. Soc.*, 2914–21 (1965); C. J. R. Adderly and F. R. Hewgill, *J. Chem. Soc. C*, 2770–4 (1968).

(4) E. Adler, K. Holmberg, and L. O. Ryrfor, *Acta Chem. Scand., Ser. B*, **28**, 888–94 (1974).

(5) Emil Kon and Edward McNeilis, *J. Org. Chem.*, **40**, 1515–7 (1975); 41, 1646–8 (1976).

(6) G. T. Burstein and G. A. Wright, *Nature (London)*, **221**, 169–70 (1969).

(7) Since the completion of our work, a report on the use of an organobismuth(V) compound to oxidize alcohols has appeared. See, D. H. R. Barton, J. P. Kitchin, and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, 1099–100 (1978). For a similar reagent, see F. Challenger and O. V. Richards, *J. Chem. Soc.*, 405–11 (1934).

(8) The hydroxy group is presumably derived from water in the reagent. The commercial sodium bismuthate we used (Ventron) contained 84% sodium bismuthate, 4% bismuth(III) oxide, and 13% water.

(9) Sodium bismuthate does not oxidize the solvent to peracetic acid.

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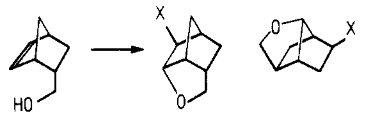
Table I. Oxidation of Olefins with Sodium Bismuthate in Acetic Acid

olefin	reacn[a] time	products	yield[b,c]
1-phenylcyclohexene	3	*cis*-2-acetoxy-1-phenylcyclohexanol	37
1-methylcyclohexene	8	1-methyl-2-acetoxycyclohexanol	21
methylenecyclohexane	7	1-(acetoxymethyl)cyclohexanol	40
α-methylstyrene	3	1-acetoxy-2-phenyl-2-propanol	39 (62)
		acetophenone	9
		α-acetoxyacetophenone	1
2,6-dimethyl-2-octene	7	2,6-dimethyl-3-acetoxy-2-octanol	21 (42)
cyclohexene	4	2-acetoxycyclohexanol	25
		3-acetoxycyclohexene	8
(*E*)-3-hexene	10	*erythro*-4-acetoxy-3-hexanol	18 (41)
(*Z*)-3-hexene	10	*threo*-4-acetoxy-3-hexanol	18
1-decene	21	1-acetoxy-2-decanol	10
		nonanal	5

[a] Reaction time in days at room temperature. [b] Yield of product (%) isolated by preparative thin-layer chromatography or distillation. [c] Isolated yield (%) corrected for recovered olefin is indicated in parentheses.

Table II. Oxidation of *endo*-2-(Hydroxymethyl)-5-norbornene



1 **2** **3**

reagents	yield, % 2	yield, % 3	X	ref
$Hg(OAc)_2/MeOH$	>95		HgOAc	*a*
$Tl_2O_3/HOAc$		46	OAc	*b*
$Tl(OAc)_3/HOAc$	21	42	OAc	*c*
$Pb(OAc)_4/C_6H_6/CaCO_3$	37	0	OAc	*d*
$NaBiO_3/HOAc$	10	35	OAc	*c*
$C_6H_5CO_3H$	>90		OH	*e*

[a] H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227–36 (1959). [b] R. M. Moriarty and H. Gopal, *Tetrahedron Lett.*, 347–50 (1972). [c] Results of the present study. [d] R. M. Moriarty and K. Kapadia, *Tetrahedron Lett.*, 1165–9 (1964). [e] H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221–6 (1959).

between these two paths, we oxidized *endo*-2-(hydroxymethyl)-5-norbornene (**1**). If epoxidation is the exclusive pathway, we would expect to obtain only tricyclic ethers **2** (X = OH, OAc), whereas if oxymetalation is intervening, we would expect predominantly the rearranged tricyclic ether **3** (X = OAc, OH). It is clear from the results in Table II that oxymetalation of **1** initially affords the cyclic ether **2** ($X = M(OAc)_n$) which, depending on the strength of the metal–carbon bond, either can be isolated (M = Hg) or can decompose to generate a carbonium ion at the metalated carbon. In nonpolar solvents such as benzene, the carbonium ion is short-lived (if ever fully generated), affording predominantly the ether acetate **2**, while in polar, ionizing solvents such as acetic acid, the carbonium ion can rearrange to the ether acetate **3**. This latter path is the predominant one followed in the sodium bismuthate oxidation. Thus the chemistry of sodium bismuthate in acetic acid resembles that of the acetates of the neighboring fifth-row $3d^{10}$ oxidants mercury, thallium, and lead.

The heterogeneous nature of the reaction and the mild, room-temperature conditions offer advantages over the more traditional reagents, lead tetraacetate and thallium triacetate. Even though the yields are only moderate, when they are corrected for recovered starting material, they are competitive with the alternate oxymetalation reagents.

Experimental Section

The following procedure for the oxidation of α-methylstyrene is representative. To a 250-mL Morton flask with a stirbar were added 5.92 g (0.05 mol) of α-methylstyrene, 100 mL of glacial acetic acid, and 16.62 g (0.05 mol) of sodium bismuthate. The reaction was permitted to stir at room temperature for 3 days. The reaction mixture was poured into ether and extracted with water followed by extraction with saturated $NaHCO_3$ until all of the acetic acid had been removed. The ether layer was then rinsed with brine, dried over anhydrous magnesium sulfate, and filtered, and the ether was removed under reduced pressure to afford 7.96 g of crude product. Column chromatography on 60 g of silica gel using hexanes and methylene chloride in an increasing gradient gave, from 1.00 g of crude product, 0.48 g (39%) of 1-acetoxy-2-phenyl-2-propanol: ^1H NMR ($CDCl_3$) δ 7.7–7.1 (m, 5 H, ArH), 4.25 (s, 2 H, CH_2OAc), 2.70 (br s, 1 H, OH), 2.02 (s, 3 H, $COCH_3$), 1.55 (s, 3 H, CCH_3).

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Registry No. 1, 15507-06-9; 2 (X = OAc), 16479-71-3; 3 (X = OAc), 35359-71-8; 1-phenylcyclohexene, 771-98-2; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6; α-methylstyrene, 98-83-9; 2,6-dimethyl-2-octene, 4057-42-5; cyclohexene, 110-83-8; (*E*)-3-hexene, 13269-52-8; (*Z*)-3-hexene, 7642-09-3; 1-decene, 872-05-9; *cis*-2-acetoxy-1-phenylcyclohexanol, 23313-43-1; 1-methyl-2-acetoxycyclohexanol, 72331-74-9; 1-(acetoxymethyl)cyclohexanol, 72331-75-0; 1-acetoxy-2-phenyl-2-propanol, 72331-76-1; 2,6-dimethyl-3-acetoxy-2-octanol, 72331-77-2; 2-acetoxycyclohexanol, 22241-34-5; 3-acetoxycyclohexene, 14447-34-8; *erythro*-4-acetoxy-3-hexanol, 64833-03-0; *threo*-4-acetoxy-3-hexanol, 72346-78-2; 1-acetoxy-2-decanol, 72331-78-3; $NaBiO_3$, 12232-99-4.

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(10) Such a sequence would require a hydroxy-metalated intermediate, since if acetoxy metalation were occurring, one would expect diacetate to be present as a reaction product.

Cycloaddition of (Trimethylsilyl)ketene with Tetraalkoxyethylenes

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We have recently reported on the cycloaddition of (trimethylsilyl)ketene with aldehydes.[1] The cycloaddition of this ketene with ketene dimethyl and diethyl acetals has also been described.[2] However, the attempted (2 + 2)

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(1) Brady, W. T.; Saidi, K. *J. Org. Chem.* **1979**, *44*, 733.

(2) Zaitseva, G. S.; Baukov, Y. I.; Mal'tsev, V. V.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1974**, *44*, 1415.

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