T-60 spectrometer using tetramethylsilane as internal standard in chloroform-d_1. Satisfactory analytical data (±0.3%) were obtained on all products. Column chromatography was performed on silica gel (Wako C300, Japan) using chloroform for elution.
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Chemisorbed Chromyl Chloride as a Selective Oxidant

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Selective oxidation is one of the most important of all chemical transformation. Many oxidants, however, remain too vigorous for such application. In this regard, one of the distinct advantages which heterogeneous reactions offer is the ability to isolate and moderate reactive species by chemisorption. Such procedures frequently have the additional virtue that intermediate products which under homogeneous conditions would prove difficult or impossible to isolate, for a variety of reasons become readily isolable under heterogeneous conditions. We have explored the possibility of moderating the reactivity of several strong oxidants by employing them as chemisorbed reagents on a high-surface, inert support. Here we report the results of one such investigation: specifically, the utility of chromyl chloride adsorbed on silica–alumina as a convenient, efficient, economical reagent for the oxidation of alcohols under neutral, nonaqueous conditions.

$$\mathrm{RCH_2OH} \xrightarrow[\mathrm{CH_2Cl_2,\ 25\ ^\circ C}]{\mathrm{CrO_2Cl_2/SiO_2{-}Al_2O_3}} \mathrm{RCHO}$$

$$\mathrm{RR'CHOH} \xrightarrow[\mathrm{CH_2Cl_2,\ 25\ ^\circ C}]{\mathrm{CrO_2Cl_2/SiO_2{-}Al_2O_3}} \mathrm{RR'CO}$$

This reaction seems to be applicable to the oxidation of primary and secondary alcohols to the respective aldehyde and ketone. A preliminary examination of the functional group compatibility of this reagent indicates that halocarbons, esters, lactones, nitriles, and ethers appear inert. Olefins, on the other hand, undergo oxidative cleavage. Thus, the same reagent will, for example, convert stilbene to benzaldehyde in 71% yield.[2]

Chromyl chloride is a vigorous oxidant whose action on organic substrates generally produces complex mixtures of products.[3] Recently, Sharpless and co-workers have demonstrated that a substantial moderation of this reactivity toward certain substrates (specifically olefins) can be achieved if these reactions are carried out at low temperatures.[4a] Further moderation can be achieved by employing a reagent derived by admixing chromyl chloride with *tert*-butyl alcohol and pyridine in methylene chloride at low temperatures.[4b] The resulting reagent is useful for the homogeneous oxidation of alcohols to aldehydes and ketones.

It is clear from the results in Table I that the chromyl chloride chemisorbed on silica–alumina is a great deal more selective than the homogeneous reagent. It is not apparent, however, whether this enhanced selectivity is a result of the inherently reduced reactivity of the chemisorbed species relative to that of chromyl chloride, or to the ability of the rigid support to immobilize a highly reactive species [e.g., Cr(IV)] so as to prevent its further possible reactions,[13a] reactions which could ultimately lead to a complex mixture of reaction products such as observed under homogeneous conditions.

Several investigators have recently employed the concept of utilizing reagents adsorbed on inert inorganic supports for organic synthesis.[5–7] Of these, three in particular bear brief comparison.[8] Lalancette and co-workers[9] have reported that primary but not secondary alcohols are oxidized to the corresponding aldehydes by a reagent purported to be CrO_3–graphite.[10] Complementing this activity are the results of Posner and co-workers,[6] who found that secondary but not primary alcohols are effectively oxidized by trichloroacetaldehyde when carried out over highly activated alumina. In contrast, the reactivity of chemisorbed chromyl chloride compares to that of the more standard reagents for alcohol oxidation[13] with the distinct advantages of preparative and manipulative convenience, similar to those recently reported

Table I. Reaction of Alcohols with Chromyl Chloride Adsorbed on Silica–Alumina[a]

Substrate	Registry no.	Product (%)[b]	Registry no.	Reaction time, h
1-Octanol	111-87-5	1-Octanal (94)	124-13-0	5
2-Octanol	123-96-6	2-Octanone (94)	111-13-7	24
2,2-Dimethylpropanol	75-84-3	2,2-Dimethylpropanal (78)	630-19-3	24
4-*tert*-Butylcyclohexanol	98-52-2	4-*tert*-Butylcyclohexanone (89)	98-53-3	6
exo-2-Norbornanol	497-37-0	2-Norbornanone (87)	497-38-1	24
1-Phenylethanol	60-12-8	Acetophenone (100)	98-86-2	5
Methyl mandelate	771-90-4	Methyl (2-keto-2-phenyl)acetate (77)	15206-55-0	
		Benzaldehyde (14)	100-52-7	3
Benzoin	119-53-9	Benzil (89)[c]	134-81-6	
		Benzaldehyde (6)		24
3-β-Cholestanol	17608-41-2	Cholestan-3-one (89)[c]	15600-08-5	5
Benzyl alcohol	100-51-6	Benzaldehyde (94)		5
4-Nitrobenzyl alcohol	619-73-8	4-Nitrobenzaldehyde (87) (83)[c]	555-16-8	5
4-Cyanobenzyl alcohol	874-89-5	4-Cyanobenzaldehyde (85)	105-07-7	5
4-Methylbenzyl alcohol	589-18-4	4-Methylbenzaldehyde (100)	104-87-0	4
2-Chlorocyclohexanol	1561-86-0	2-Chlorocyclohexanone (87)	822-87-7	24
2-Bromocyclohexanol	24796-87-0	2-Bromocyclohexanone (95)	822-85-5	24
2-Bromo-1-indanol	5400-80-6	2-Bromo-1-indanone (77)	1775-27-5	12

[a] Reactions carried out at 25 °C in methylene chloride solvent. Substrate to oxidant ratio: 0.10 mol to ~180 g of CrO_2Cl_2–SiO_2–Al_2O_3 reagent (2.92% Cr by weight[15]). [b] Yields, unless otherwise indicated, were determined by GLC or HPLC. Products were identified by comparison of their IR and mass spectra with those of authentic samples as well as GLC retention times and melting points where applicable. [c] Value based on isolated yield.

by Cainelli and co-workers for the oxidation of alcohols by chromic acid on anion exchange resins.[14]

Experimental Section

In a typical procedure, a solution of CrO_2Cl_2 (10.0 g) in methylene chloride (100 mL) is added with stirring to a slurry of SiO_2–Al_2O_3 (90.0 g, Grace Davison No. 135) in methylene chloride (150 mL). After stirring for an additional 5 min, the yellow-orange solid was collected by suction filtration on a fritted-glass funnel and subsequently dried under reduced pressure. The resulting solid can be used immediately or stored indefinitely if reasonable precautions against moisture are observed.

The following description represents a typical oxidation procedure. Two grams of the above reagent (1.10 mmol of Cr as determined by elemental analysis[15]) are placed in a flask along with 20 mL of methylene chloride and a Teflon-coated stirrer bar. A solution of 1-octanol (0.143 g, 1.10 mmol) in methylene chloride (5 mL) is added and the flask equipped with a drying tube. The resulting mixture is stirred for 5 h before adding 0.5 mL of methanol and filtering. The residual solids are rinsed with two 10-mL portions of methylene chloride and the combined clear, colorless filtrates analyzed directly by GLC. The yield of 1-octanal is 94%; none of the corresponding carboxylic acid is observed. A summary of the results obtained with other representative substrates is presented in Table I.

Registry No.—Chromyl chloride, 14977-61-8.

References and Notes

(1) Supported by the National Institutes of of Health (AM-18713-01).

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Dynamic Carbon-13 Nuclear Magnetic Resonance Spectra of Benzobullvalene and *o*-Toluobullvalene

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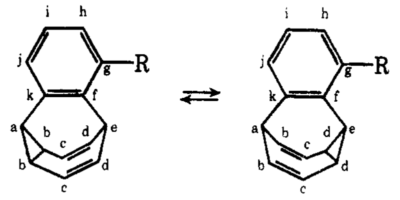
The factors which control the rate of the Cope rearrangement in bullvalene and related compounds are a topic of considerable interest.[1] The elegant work of Oth[2] and Günther[3] has shown that variable temperature ^{13}C NMR is an ideal tool for such investigations. The synthesis and dynamic ^{13}C NMR study of benzobullvalene (1, R = H) and *o*-toluobullvalene (1, R = Me) is now reported.



1 2

The synthesis of these compounds was based on Doering's rational scheme for the preparation of bullvalene[4] employing the benzyne adduct of tropone[5] as a starting material. Eisenstadt[6] has recently published an analogous procedure. The low- and high-temperature ^{13}C NMR chemical shifts and their assignments are given in Table I. Peaks were assigned on the basis of intensity, chemical shift, multiplicity in off-resonance proton decoupled spectra, and by following their pairwise coalescence as temperature was increased. The assignment of carbons a and e in *o*-toluobullvalene is critical for the assignment of the major isomer for this nondegenerate case. In benzobullvalene, the cyclopropane carbon, 1a or 2e, is upfield of the methine carbon, 1e or 2a, based on the known assignment of bullvalene.[2,3] The introduction of the methyl group in *o*-toluobullvalene results in an upfield shift of 5.9 ppm in the high field peak of minor isomer as the only significant shift change. Based on the well-established,[7] γ-upfield shift of methyl groups, the major isomer is assigned structure 2, R = Me. Based on peak intensities in the low temperature spectrum, the equilibrium constant was found to be 1.6 ± 0.3 at −59 °C. Based on the population averaged chemical shifts at 143 °C, an equilibrium constant of 1.1 ± 0.3 is obtained. The preference for the methyl group on the same side of the molecule as the cyclopropane is consistent with the data recently reported for the methyl group in 9-ethylidenebarbaralene.[8] The reason for this preference remains obscure.

The dynamic parameters for the Cope rearrangement in benzobullvalene were determined by variable temperature carbon-13 NMR. A program[9] employing an equal population two site exchange process was used to calculate the theoretical line shapes. The large spread of chemical shift differences between exchanging carbons permitted observation of line broadening phenomena from −50 to 120 °C. The activation parameters are shown in Table II together with those reported for bullvalene. It is perhaps worth noting that the factor of 2 rate increase (0 °C) induced by replacing a double bond in bullvalene with a benzo group is the smallest structurally induced perturbation on the rate of the degenerate Cope reaction in bridged homotropilidenes.

Our plans to examine a range of substituted benzobullvalenes were thwarted by the observation that the reaction of tropone with 3-chloro- and 3-methoxybenzyne (generated from the 6-substituted anthranilic acids) gave substituted cycloheptatrienylbenzofuran derivatives.

Experimental Section[10]

Proton NMR spectra were recorded on Varian A-60 and XL-100-15 spectrometers in $CDCl_3$. Chemical shifts are reported in δ units from internal Me_4Si. IR spectra were recorded in KBr disks on Perkin-Elmer 257 and 727 spectrometers and mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6D spectrometer. Microanalyses were performed by the Purdue Microanalytical Service. Melting points are uncorrected.

Tropone,[11] 6,7-benzobicyclo[3.2.2]nonatrien-2-one,[12] and 6,7-benzobicyclo[3.2.2]nonatrien-2-ol[13] were prepared by previously published methods. Details of an improved procedure for the preparation of benzobullvalene are given in the microfilm edition. The product had mp 109–110 °C (lit.[6,14] 89, 110–111 °C). Spectral details for the *o*-toluobullvalene intermediates may also be found in the microfilm edition.

Methyl-6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one (I). In a 600-mL beaker equipped with a stirring bar and thermometer 3-methylanthranilic acid (32.0 g, 0.212 mol) was dissolved in dry THF (250 mL). After cooling in an ice bath Cl_3CCO_2H (0.3 g) dissolved in