thinking on pseudorotation in pentacovalent trigonalbipyramidal molecules has been based on these early papers. Later it was shown[3,4] that ligand exchange occurred when the temperature was raised above room temperature and that the barrier to pseudorotation in compounds such as $(CH_3)_2PF_3$ and $(C_6H_5)_2PF_3$ was in the range 15-20 kcal/mol. Since the appearance of the original two papers from Muetterties' laboratory a large number of papers have appeared on pseudorotation in compounds of the type R_2PF_3 and R_3PF_2.[3-5]

In contrast to the large amount of research on pseudorotation in organophosphorus compounds, very little has been done with organoarsenic compounds. Muetterties[2] reported that the ^{19}F NMR spectrum of $(C_6H_5)_2AsF_3$ in toluene solution consists of a doublet and a triplet of relative intensity 2:1, and that the spectrum was invariant over large changes in temperature and concentration. Unfortunately the preparation of the R_2AsF_3 compounds was not described nor were the compounds characterized other than by their NMR spectra. As far as we are aware no work other than that reported by Muetterties has been performed on the NMR spectra of compounds of the type R_2AsF_3.

A number of attempts to prepare $(C_6H_5)_2AsF_3$ have been made in this laboratory. The two successful syntheses have involved the fluorination of either $(C_6H_5)_2AsH$ or $(C_6H_5)_2AsCl$ with SF_4 by means of standard vacuum line techniques. The product of either synthesis was a white crystalline solid, mp 94-96 °C, in a preheated bath after several recrystallizations from carbon tetrachloride. The carbon, hydrogen, and arsenic analyses agreed closely with the theoretical values. In addition this compound displayed a strong As-F stretching band at 470 cm^{-1} in the IR.

Diphenyltrifluoroarsorane is extremely sensitive to traces of moisture, and all manipulations must be carried out under rigidly anhydrous conditions using either a drybox or Schlenk tube conditions. The solvent (CCl_4) was dried by refluxing over activated molecular sieves and storing the distilled solvent over activated sieves. Exposure to air for even a short time resulted in loss of fluorine as shown by both the NMR spectrum and elemental analysis.

The ^{19}F spectrum of the pure compound in methylene chloride in Teflon tubes,[7] after several recrystallizations under anhydrous conditions, consisted of a slightly broadened singlet at 69.1 ppm upfield from $CFCl_3$. This spectrum was essentially unchanged (except for small chemical shifts) in a wide variety of solvents, nor was it changed by the addition of NaF to the solution. When cooled to −90 °C in methylene chloride the singlet was at least as sharp as at room temperature; no splitting was ever observed. These results suggest that, unlike the analogous fluorophosphorane, the arsenic compound is undergoing fast ligand exchange, both at room temperature and at −90 °C. This may result from a Berry pseudorotation with the larger arsenic atom providing a lower energy barrier, or it may involve an intermolecular exchange process. Moreland and co-workers[6] have demonstrated that exchange in tribenzylarsenic difluoride involves an intermolecular exchange.

While we have taken precautions to exclude moisture and to avoid impurities in our samples there is no guarantee that our results, which differ from those reported earlier by Muetterties, are not caused by catalysis effected by impurities. We have made diphenyltrifluoroarsorane a number of times by two different methods and in none of our products have we ever seen the NMR coupling pattern reported by Muetterties and co-workers. It is obvious that much more work is required on ligand exchange in fluoroarsoranes.

Acknowledgment. The authors wish to acknowledge helpful discussions with Dr. C. G. Moreland and Dr. L. D. Freedman.

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Oxidation of Ethers via Hydride Abstraction: a New Procedure for Selective Oxidation of Primary, Secondary Diols at the Secondary Position[1]

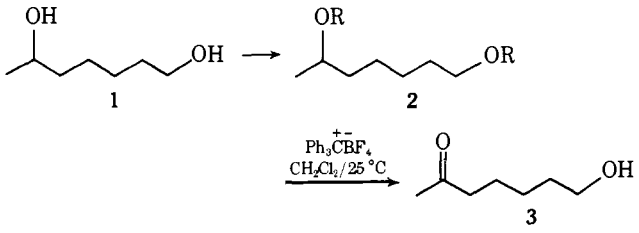
Sir:

Many new methods have been recently added to the long list of procedures for the oxidation of alcohols to carbonyl compounds. New developments in this area should be designed to effect selective oxidation in polyhydroxylated molecules. We wish to report such a method, namely, the totally selective oxidation of primary, secondary diols at the secondary center by a hydride abstraction process.

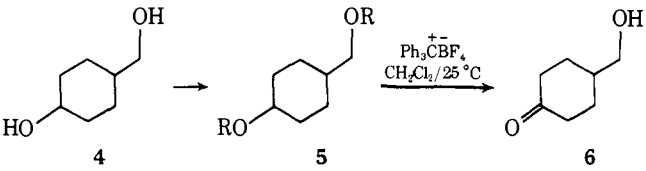
Several techniques have been reported in the literature for selective oxidation of a secondary alcohol. Johnson and co-workers[2] reported that treatment of various tricyclic primary, secondary diols with *N*-bromoacetamide afforded fair yields of the keto alcohols. More recently, Wicha and co-workers[3] have observed that various steroidal diols undergo oxidation only at the most accessible secondary center in preference to primary ones in the presence of chlorine and pyridine. Many other methods have also been reported,[4] including selective protection of the primary hydroxyl function, oxidation, and removal of the protecting group. This three-step method is hampered quite often by the inability to cleanly protect the primary hydroxyl group in the presence of a secondary one, a result which often requires chromatographic separation of the desired material from its by-products.

Our procedure utilizes the oxidation technique we developed recently which involves the treatment of trimethylsilyl or *tert*-butyl ethers of alcohols with triphenylcarbenium (trityl) salts.[5] Doyle has made similar observations in the disproportionation of trityl ethers of alcohols by a cationic chain reaction process.[6] We reasoned that, since these oxidations proceed via initial hydride abstraction followed by loss of the group on oxygen, oxidation at a secondary center should be much faster than at a primary center and our initial studies seemed to corroborate this reasoning.[5] Thus we decided to apply this method to primary, secondary diols.

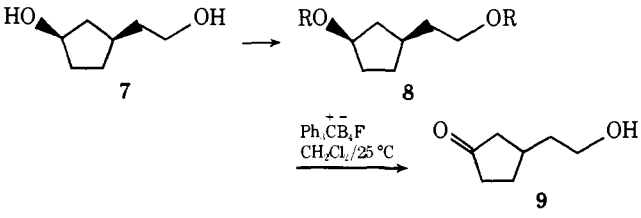
1,6-Heptanediol could be converted into the bistrityl ether **2a** by treatment with trityl chloride in pyridine in quantitative yield. In a like manner 4-hydroxymethylcyclohexanol (**4**) and 3-(2-hydroxyethyl)cyclopentanol (**7**) could be transformed into the bistrityl derivatives **5a** and **8a**, respectively, in quantitative yield. When the bistrityl ether of 1,6-heptanediol **2a** was treated with trityl tetrafluoroborate in methylene chloride at room temperature for 15 min, the desired product **3**, 7-hydroxy-2-heptanone, was isolated in the pure state in 91% yield.



Yield, %		Time/yield, %	Overall yield, %
100	a, R = CPh_3	15 min/91	91
84	b, R = CMe_3	30 min/76	64
100	c, R = $SiMe_3$	10 h/~20	~20



Yield, %		Time/yield, %	Overall yield, %
100	a, R = CPh_3	15 min/79	79
77	b, R = CMe_3	6 h/60	46
100	c, R = $SiMe_3$	-	-



Yield, %		Time/yield, %	Overall yield, %
100	a, R = CPh_3	15 min/85	85
54	b, R = CMe_3	1 h/40	22
100	c, R = $SiMe_3$	-	-

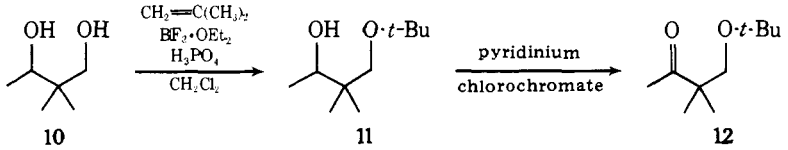
The oxidation of the bistrityl ether **5a** under conditions identical with those for **2a** afforded the desired keto alcohol **6**, 4-hydroxymethylcyclohexanone, in 79% isolated yield. The analogous bistrityl ether in the cyclopentane series **8a** also afforded 85% of the desired product **9**, 3-(2-hydroxymethyl)-cyclopentanone, when subjected to the same conditions as for **2a**.

In a typical procedure the bistrityl ether of 1,6-heptanediol **2a** (1.52 mmol) was allowed to stir for 15 min with trityl tetrafluoroborate (1.52 mmol) in 15 ml of methylene chloride at room temperature under nitrogen. Methylene chloride and saturated aqueous sodium bicarbonate were added and the layers separated. After drying (Na_2SO_4) and concentration in vacuo, the crude product mixture in a small volume of dry benzene was applied to a dry column of Davison silica gel (15 g). The column was developed with dry benzene and allowed to stand at room temperature for 24 h. Elution of the column with benzene yielded triphenylmethane and triphenylcarbinol. Further elution with 5% ethanol in ethyl acetate afforded the product 7-hydroxy-2-heptanone (1.39 mmol) in 91% yield.

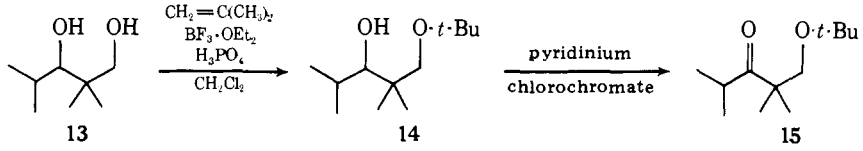
The bis-*tert*-butyl **2b** and bistrimethylsilyl **2c** ethers of 1,6-heptanediol could also be prepared by known methods in the yields indicated. Similarly, the diols **4** and **7** could be transformed into their bis-ether derivatives **5b–c** and **8b–c**, respectively, in the yields indicated.

Oxidation of the bis-*tert*-butyl ether **2b** with trityl salt was complete in 30 min, but the reaction mixture was stirred for 8 h to effect hydrolysis of the primary ether. Silica gel chromatography provided **3** in 76% isolated yield. The two corresponding bis-*tert*-butyl ethers, **5b** and **8b**, required somewhat longer times for complete oxidation/hydrolysis and furnished significantly lower yields of the desired products, **6** and **9**, respectively. The oxidation of the bissilyl ether **2c** and of the other bissilyl ethers **5c** and **8c** with trityl salt did not proceed cleanly. In the case of **2c**, oxidized products accounted for only 20% of the material. In all cases oxidation of the bis-*tert*-butyl ethers gave much better results than the bissilyl ethers. However, in all these systems the method of choice for oxidation is via the bistrityl ether.

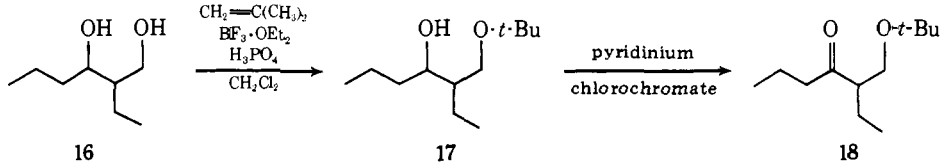
When we attempted to use the bis-*tert*-butyl ether oxidation scheme to oxidize some 1,3-diols, we were totally successful but for a different reason, namely, only the primary *tert*-butyl ether could be formed. For example, when 2,2-dimethyl-1,3-butanediol (**10**) was treated with isobutylene in the presence of boron trifluoride etherate and anhydrous phosphoric acid in methylene chloride,[7] the exact conditions for the formation of the bis ethers **2b**, **3b**, and **4b**, only the mono-*tert*-butyl ether **11** was obtained in 90% yield. Likewise, when other 1,3-diols, e.g., 2,2,4-trimethyl-1,3-pentanediol, **13**, and 2-ethyl-1,3-hexanediol, **16**, were treated under identical conditions only the mono-*tert*-butyl ethers, **14** and **17**, were obtained in high yields. These readily available mono-*tert*-butyl ethers (**11**, **14**, **17**) could then be oxidized efficiently by pyridinium



Yield 90% Yield 91% Overall yield 82%



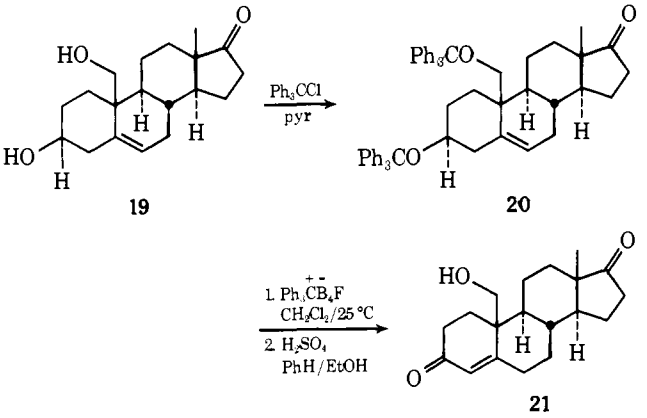
Yield 90% Yield 98% overall yield 88%



Yield 92% Yield 93% Overall yield 86%

chlorochromate[8] to afford the ketones **12, 15,** and **18** in very high yields. Thus the overall process for these 1,3-diols results in high yields of the keto alcohol derivative without any chromatographic separation.

One additional diol was successfully oxidized by the bistrityl ether technique. The bistrityl ether **20** of 5-androsten-3β,19-diol-17-one (**19**)[9] could be oxidized by our general procedure. In this case, the strong acid necessary to hydrolyze the primary ether also caused conjugation of the enone system, so that keto alcohol **21** was obtained in good yield. However, this case is somewhat biased toward oxidation at the secondary center due to the extreme steric crowding about the primary ether center (C-19). For this reason, we do not feel this case is a fair test of the general method even though the desired reaction proceeds.



Not all diols could be successfully oxidized by our procedure. For example, straight chain 1,2-diols, e.g., octane-1,2-diol, gave poor results. Despite this limitation, we feel this method does represent a general solution to the problem of selective oxidation of primary, secondary diols.

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Restricted Rotation of σ-Alkyl Intermediates on a MoS_2 Catalyst

Sir:

The coordinative unsaturation of active sites is an important property of oxide and sulfide catalysts[1,2] as well as of homogeneous catalysts.[3] A proposal has been given that both the isomerization of olefins and the intermolecular hydrogen atom exchange between olefins may occur on the sites to which is bound one hydrogen atom and which have one coordinative vacancy, whereas the hydrogenation of olefins proceeds only on the active sites having three degrees of coordinative unsaturation.[1,2] To shed light on the intermediates formed during the isomerization and of the hydrogen exchange reaction of olefins, a mixture of undeuterated and perdeuterated butenes was allowed to react over a MoS_2 catalyst and the monoexchanged d_1 species formed in these reactions were submitted to microwave spectroscopic analysis. The MoS_2 used here has $2H$ (hexagonal) structure (shown by x-ray diffraction) and a BET surface area of 15 m^2/g. The impurities by atomic absorption analysis were Fe, 0.02; Mg, 0.0015; Ca, 0.0077; Na, 0.012; Mn, 0.0003; Cr, <0.0001; and K, <0.1%.

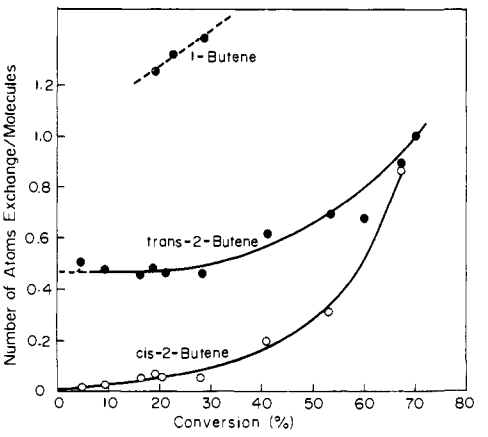
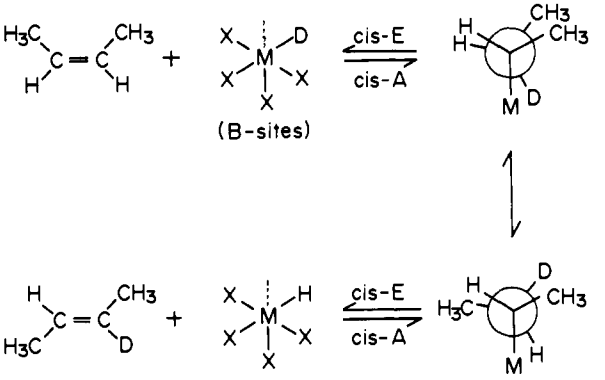


Figure 1. Number of exchanged hydrogen atoms per molecule in the coisomerization of *cis*-but-2-ene-d_0 and *cis*-but-2-ene-d_8 (1:1) in the presence of H_2 and D_2 (1:1) at room temperature.

Figure 1 shows the results of the coisomerization of *cis*-but-2-ene-d_0 and *cis*-but-2-ene-d_8 (1:1) at room temperature, in which the number of hydrogen atoms which have been exchanged was calculated by the method of Hightower and Hall.[4]

$$\text{H atoms exchanged per molecule} = \sum_{i=1}^{4} iN_i + \sum_{i=5}^{8} (8 - i)\ N_i$$

where N_i is the mole fraction of each species containing i deuterium atoms. As shown in Figure 1, the number of exchanged hydrogen atoms per *trans*-but-2-ene molecule is very close to 0.5. This fact indicates that the cis–trans isomerization reaction occurs only with stereospecific hydrogen addition and elimination, which may be analogous to the pure cis stereochemistry observed in the cis addition of hydrogen to methyl acetylene over the MoS_2,[5] where "cis-A" and "cis-E" indicate



cis addition and cis elimination of hydrogen. As the *trans*-but-2-ene-d_1 is inactive for microwave spectroscopic analysis, the *cis*-but-2-ene-d_1 formed in the coisomerization of *cis*-but-2-ene-d_0 and *cis*-but-2-ene-d_8, which was brought about