It should be noticed the position of the saddle point moves out monotonically toward the $F + H_2$ channel as this height decreases. This should be expected in general for nonthermoneutral reactions[18] and should be a caution against emphasizing[11] a prediction of the geometry of the saddle point when its height is not predicted correctly.

Acknowledgment. This work was supported in part by the National Science Foundation under Grant No. GP-28684. The author is grateful to Professor Fritz Schaefer for discussions.

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[18] See, *e.g.*, G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955); M. H. Mok and J. C. Polanyi, *J. Chem. Phys.*, **51**, 1451 (1969); and C. A. Parr and D. G. Truhlar, *J. Phys. Chem.*, **75**, 1844 (1971).

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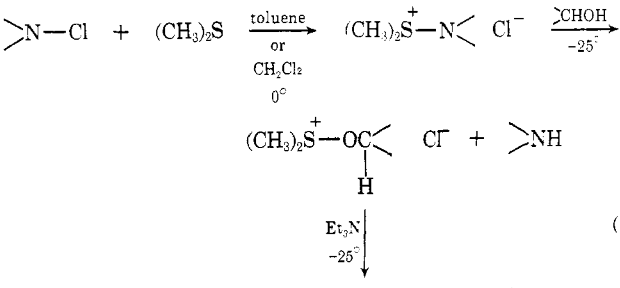
A New and Highly Effective Method for the Oxidation of Primary and Secondary Alcohols to Carbonyl Compounds

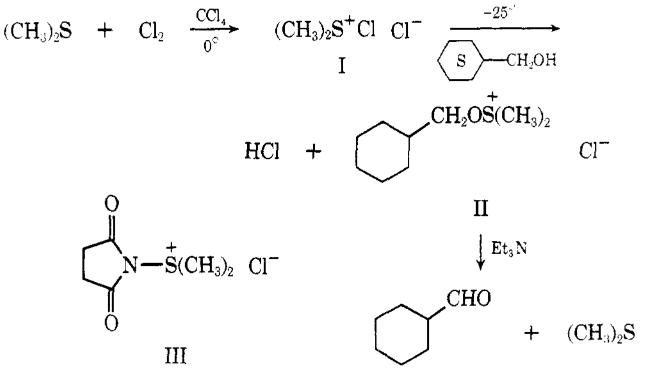
Sir:

We report here a new process for the oxidation of alcohols to ketones or aldehydes which is operationally simple, highly selective, and efficient. It is expected that the method will find widespread use and that in many instances it will be found superior to currently important procedures such as those using the reagents CrO_3–pyridine complex,[1] CrO_3–acetone,[2] and dimethyl sulfoxide with various coreactants.[3-5] An overall representation of the new method, which is clearly related to the dimethyl sulfoxide based processes, is given in sequence 1.



(1)

The long-known complexes which result from the reaction of halogens with sulfides,[6] $R_2S^+Hal\ Hal^-$, might be expected to react with an alcohol to form a type of sulfoxonium complex, $R_2S^+OCH{<}\ Hal^-$,[6b] which judging from previous work[3-5] should under suitable conditions undergo elimination to form a carbonyl compound. This process would effectively allow an overall transformation such as: $RR'CHOH + Cl_2 \rightarrow RR'CO + 2HCl$, which is mediated by a sulfide. The operability of this scheme has now been demonstrated. For example, treatment of dimethyl sulfide in carbon tetrachloride at 0° with 1 equiv of chlorine in carbon tetrachloride at 0° results in rapid formation of the partially insoluble complex I, which when cooled to −25° (Dry Ice–carbon tetrachloride bath) and treated with cyclohexylcarbinol for 2 hr at −25° with stirring is converted to the sulfoxonium complex II. Addition of 2 equiv of triethylamine, removal of the cooling bath, and isolation after 5 min affords pure cyclohexylcarboxaldehyde in *ca.* 80% yield after distillation.



The oxidation of cyclohexylcarbinol can be effected even more cleanly and efficiently (93% yield) using the recently reported complex III from dimethyl sulfide and *N*-chlorosuccinimide[7,8] under carefully controlled conditions. Most of this work has been performed using the complex III, since the use of *N*-chlorosuccinimide for small-scale laboratory work is convenient, since the formation of hydrogen chloride is avoided (in contrast to the use of I), giving a milder and probably more generally useful method, and, finally, since the reaction products are somewhat cleaner.

The simplicity and the key details of the new oxidation process are illustrated by the following procedures for the preparation of a ketone and an aldehyde.

A. 4-*tert*-Butylcyclohexanone. To a stirred solution of 400 mg (3.0 mmol) of *N*-chlorosuccinimide in 10 ml of toluene (analytical grade) was added at 0° 0.3 ml (4.1 mmol) of methyl sulfide under argon. A white precipitate appeared immediately after addition of the sulfide. The mixture was cooled to −25° (carbon tetrachloride–Dry Ice), and a solution of 312 mg (2.00 mmol) of 4-*tert*-butylcyclohexanol (mixture of cis and trans) in 2 ml of toluene was added dropwise. The stirring was continued for 2 hr at −25°, and then a solution of 303 mg (3.0 mmol) of triethylamine in 0.5 ml of toluene was added dropwise. The cooling bath was removed and after 5 min, 20 ml of ether was added. The organic layer was washed with 5 ml of 1% aqueous hydrochloric acid and twice with 15 ml of water. Removal of dried (magnesium sulfate) solvents produced 310 mg (∼100%) of 4-*tert*-butylcyclohexanone as white

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[1] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

[2] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *ibid.*, 2555 (1953).

[3] K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661 (1965); **88**, 1762 (1966).

[4] J. R. Parikh and W. von E. Doering, *ibid.*, **89**, 5505 (1967).

[5] W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967).

[6] See, for example, (a) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. II, Chemical Publishing Co., New York, N. Y., p 48, and also (b) H. Meerwein, K.-F. Zenner, and R. Gipp, *Justus Liebigs Ann. Chem.*, **687**, 67 (1965). The question of tetracovalent or sulfonium sulfur in these complexes merits further study, but is not crucial to the present application.

[7] E. Vilsmaier and W. Sprügel, *Tetrahedron Lett.*, 625 (1972).

[8] Other examples of azasulfonium salts have been reported by (a) P. G. Gassman, G. Gruetzmacher, and R. H. Smith, *ibid.*, 497 (1972), and (b) C. R. Johnson, C. C. Bacon, and W. D. Kingsbury, *ibid.*, 501 (1972). The latter group has also reported the isolation of unstable sulfoxonium salts from alcohols and the complexes of sulfides with *N*-chlorobenzotriazole.

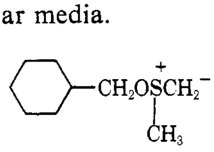
plates which melted at 44–47° (an authentic sample from Aldrich Chemical Co. had mp 45–50°). The infrared and nmr spectra were identical with those of an authentic sample, and the nmr spectrum showed that no more than 1% of the methylthiomethyl ether of 4-*tert*-butylcyclohexanol was present. Vapor chromatographic analysis indicated a yield of 97% (xylene as internal standard with a 10% SE-30, 10-ft column).

B. Octanal. The complex III (3 mmol) was generated following the procedure described above. To this stirred suspension of III was added a solution of 260 mg (2.0 mmol) of 1-octanol in 1 ml of toluene at −25°. After stirring at −25° for 90 min, a solution of 303 mg (3.0 mmol) of triethylamine in 1 ml of toluene was added. The cold bath was then removed, and after 5 min, 20 ml of ether was added. The organic layer was washed with 5 ml of 1% aqueous hydrochloric acid and then twice with 15 ml of water. The organic layer was dried (magnesium sulfate) and concentrated under reduced pressure to 10 ml and analyzed by vapor phase chromatography (10% SE-30, 10-ft column with xylene as the internal standard) (96% yield). Removal of all solvents under reduced pressure produced 250 mg of 1-octanal as a colorless liquid which was spectroscopically identical with an authentic sample.

Using the method detailed above, benzyl alcohol and 2-octanol were converted respectively to benzaldehyde (90% yield) and 2-octanone (91% yield). 1,2-Diphenyl-1,2-propanediol gave 2-hydroxy-1,2-diphenyl-1-propanone in 86% yield indicating that the sulfonium method may be valuable for the avoidance of C–C bond cleavage in the oxidation of *sec,tert*-α-glycols to α-ketols.

An important limit on the scope of the new oxidation process has been observed, however. Benzhydrol and 2-cyclohexenol sufferek replacement of hydroxyl by chlorine instead of oxidation using III under the standard conditions. The conversion of alcohols to halides is very efficient for such cases involving alcohols which correspond to stabilized carbocations.[9,10] Fortunately the oxidation of allylic or benzylic alcohols is readily effected by other mild, highly selective oxidizing agents, including manganese dioxide and various quinones, and consequently there is no pressing need for the sulfonium reagents in such cases.

Still another reaction may occur in more polar media, *viz.* the transformation of the alcohol ROH to the corresponding methylthiomethyl ether $ROCH_2SCH_3$. Thus, although cyclohexylcarbinol is converted cleanly to the corresponding aldehyde using complex III at −25° in *toluene* with less than 1% of methylthiomethyl ether formation, the methylthiomethyl ether is formed to the extent of *ca.* 18% in *methylene chloride* at −25° and 45% in *methylene chloride–dimethyl sulfoxide* (1:1) at −25°. It seems likely that the ylide IV is an intermediate[11] in the formation of the methyltoiomethyl ether and that its formation and/or further reaction can be avoided in nonpolar media.



IV

The oxidation process which is described herein should be extremely useful for complex or polyfunctional molecules, the reaction conditions being so mild as to minimize the possibility of involvement of most functional or protecting groups. As is clear from the examples cited above the yields of carbonyl compounds are remarkably high and there is little variation in optimal conditions.[12]

We are currently exploring other applications of reagents such as III, for example to carboxyl activation. The use of inexpensive halogen-derived reagents such as I for large scale oxidation is also under study.

Acknowledgment. This research was supported in part by grants from the National Science Foundation and the National Institutes of Health.

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[9] The transformation of alcohols to halides will be discussed in detail in a separate publication: E. J. Corey, C. J. Kim, and M. Takeda, *Tetrahedron Lett.*, in press.

[10] Clearly heterolysis of a sulfoxonium intermediate, $(CH_3)_2S^+$-$ORCl^-$, to form R^+Cl^- and $(CH_3)_2SO$ is expected to compete favorably with carbonyl-forming elimination if R^+ is sufficiently stabilized and to lead to chloride. The study of oxidation *vs.* chloride formation thus can provide a simple, relative, and interesting measure of carbocation stabilization. For example, cholesterol is converted by III to Δ^5-cholesten-3-one and not to chloride.

[11] K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5670 (1965). Methyl thiomethyl ethers are commonly found as by-products in oxidations using dimethyl sulfoxide based reagents. See also C. R. Johnson and W. G. Phillips, *ibid.*, **91**, 682 (1969).

[12] A number of bases other than triethylamine have been used in oxidations of alcohols with the reagent III, including 1,5-diazabicyclo-[4.3.0]nonene-5 and 1,4-diazabicyclo[2.2.2]octane, but triethylamine appears to be the amine of choice.

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Photosensitized Aquation of the Hexacyanochromate(III) Ion. Evidence against the Doublet Mechanism

Sir:

Two principal mechanisms have been proposed in order to account for the photochemistry of Cr(III) complexes.[1] The first mechanism[2] assumes that the lowest spin-forbidden excited state (${}^2E_g$, Figure 1) is that one responsible for the photoreactivity, whereas the alternative mechanism[3] involves the lowest quartet excited states (${}^4T_{2g}$ and ${}^4T_{1g}$, Figure 1) as direct precursors to the photochemical reactions. Neither direct photolysis[1] nor sensitization experiments[4–6] has as yet given a definitive answer to the above alternative, whereas quenching experiments carried out on $Cr(NH_3)_2(NCS)_4^-$ have clearly shown that its photoaquation originates, at least in part, from the lowest quartet excited state.[7] These latter experiments as well as some studies[7,8] on the temperature dependence of the phosphorescent lifetime for some

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[1] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970.

[2] R. A. Plane and J. P. Hunt, *J. Amer. Chem. Soc.*, **79**, 3343 (1957); H. L. Schläfer, *J. Phys. Chem.*, **69**, 2201 (1965).

[3] A. W. Adamson, *ibid.*, **71**, 798 (1967).

[4] A. W. Adamson, J. E. Martin, and F. D. Camassei, *J. Amer. Chem. Soc.*, **91**, 7530 (1969); J. E. Martin and A. W. Adamson, *Theor. Chim. Acta*, **20**, 119 (1971).

[5] V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, *J. Amer. Chem. Soc.*, **93**, 339 (1971).

[6] E. Zinato, P. Tulli, and P. Riccieri, *J. Phys. Chem.*, **75**, 3504 (1971).

[7] S. N. Chen and G. B. Porter, *Chem. Phys. Lett.*, **6**, 41 (1970).

[8] F. D. Camassei and L. S. Forster, *J. Chem. Phys.*, **50**, 2603 (1969).