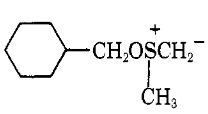
plates which melted at 44–47° (an authentic sample from Aldrich Chemical Co. had mp 45–50°). The infrared and nmr spectra were identical with those of an authentic sample, and the nmr spectrum showed that no more than 1% of the methylthiomethyl ether of 4-*tert*-butylcyclohexanol was present. Vapor chromatographic 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.



$C_6H_{11}CH_2O\overset{+}{S}(CH_3)CH_2^-$

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).

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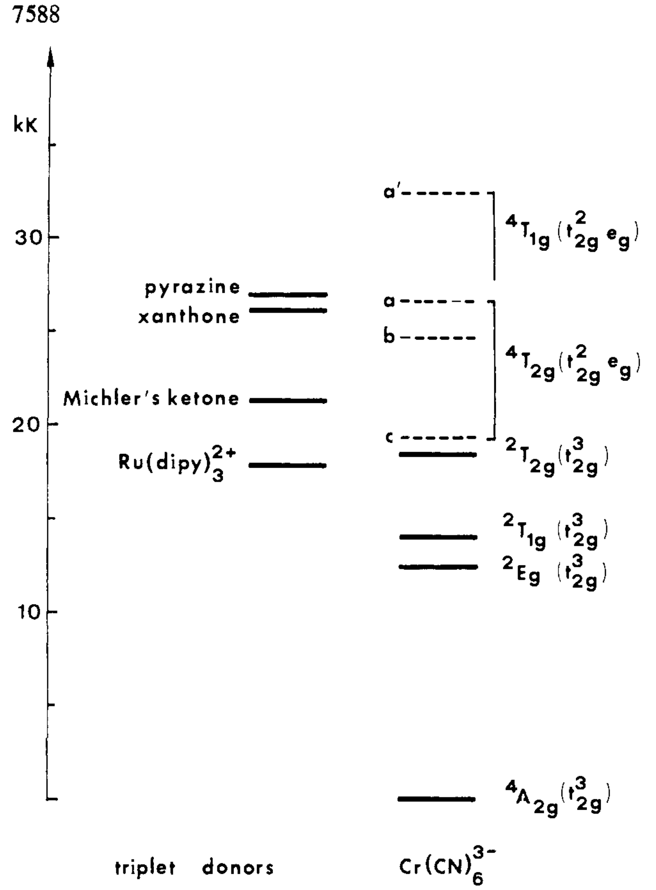

Figure 1. Energy level diagram showing the triplet energy of the donors used and the various levels of $Cr(CN)_6^{3-}$. The strong-field electronic configuration of each $Cr(CN)_6^{3-}$ level is also shown in parentheses. As discussed in the text, the energy locations of the zero vibrational levels of the quartet excited states of $Cr(CN)_6^{3-}$ are uncertain. *a* and *a'* are the energies of the absorption maxima of $^4T_{2g}$ and $^4T_{1g}$. *b* and *c* are upper and lower limiting values for the zero vibrational level of $^4T_{2g}$ as deduced from the half-width of the absorption band and the Stokes shift between absorption and emission, respectively. From the present sensitization study, the reactive state of $Cr(CN)_6^{3-}$ is identified as the $^4T_{2g}$ state (see text).

Cr(III) complexes have also suggested that $^4T_{2g}$ and ^2E_g may be in thermal equilibrium, so that it might be impossible to draw definitive conclusions on their specific role with respect to photochemistry.[9] The $^2E_g \rightsquigarrow {}^4T_{2g}$ back intersystem crossing, however, is negligible for $Cr(CN)_6^{3-}$,[8] so that this complex, which undergoes a simple photoaquation reaction (eq 1) both

$$Cr(CN)_6^{3-} + H_2O \xrightarrow{h\nu} Cr(CN)_5H_2O^{2-} + CN^- \qquad (1)$$

in water[10] and in ethanol–water mixtures,[11] is a very suited one for photosensitization experiments which could hopefully give some definitive information.

The potential donors used were those shown in Figure 1. The solvent was water for pyrazine and $Ru(dipy)_3^{2+}$ and ethanol–water mixtures for xanthone and Michler's ketone. None of the donors gave any disturbing thermal or photochemical reaction under our experimental conditions (7°, deaerated solutions). The release of CN^- (reaction 1) was measured by a liquid-membrane ion-selective electrode.

Pyrazine and xanthone were found to photosensitize the aquation of $Cr(CN)_6^{3-}$, whereas Michler's ketone and $Ru(dipy)_3^{2+}$ did not. Since the fluorescent emission of pyrazine was unaffected by $Cr(CN)_6^{3-}$, the observed sensitization process was due to the triplet state of the donor. In spite of the lack of any sensitization effect by $Ru(dipy)_3^{2+}$ on reaction 1, the intense phosphorescent emission of this last molecule was quenched by $Cr(CN)_6^{3-}$ at a rate close to the diffusion-controlled one. Moreover, $Ru(dipy)_3^{2+}$ was found to sensitize[12] the $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence of $Cr(CN)_6^{3-}$, so that an efficient energy transfer did occur even in the case of this donor.

The energy levels of the donors[13–15] and $Cr(CN)_6^{3-}$ are shown in Figure 1. Spin-conservation rules[16] permit transfer from donor triplets to both quartet and doublet states of the acceptor. The zero-vibrational levels of the doublet states of $Cr(CN)_6^{3-}$ are well known from spectroscopic studies.[17] As far as the quartet excited states are concerned, the situation is complicated by noticeable distortions of these states with respect to the ground state[1] (see below). Since pyrazine and xanthone sensitize the aquation of $Cr(CN)_6^{3-}$ whereas Michler's ketone and $Ru(dipy)_3^{2+}$ do not, one can conclude that *none of the doublet states can be responsible for the photoaquation. Thus, the doublet mechanism hypothesis*[2] *has to be definitively discarded as far as* $Cr(CN)_6^{3-}$ *is concerned.*[18] The precursor to the photochemistry may now be identified as the $^4T_{2g}$ state whose zero vibrational level, as previously mentioned, cannot be defined spectroscopically. From the half-width of the absorption band one can only say that such a level must lie at least 2000 cm^{-1} lower than the energy of the absorption maximum (*a* and *b*, Figure 1). Judging from the Stokes shift between the $^4A_{2g} \rightarrow {}^4T_{2g}$ absorption (26,600 cm^{-1}) and $^4T_{2g} \rightarrow {}^4A_{2g}$ emission ($\sim$12,000 cm^{-1}) maxima,[19] one may infer that the zero vibrational level of $^4T_{2g}$ should be at about 19,300 cm^{-1} (*c*, Figure 1). In reality, this last value may well represent a lower limiting value since the potential energy surface of the excited state should be flatter than that of the ground state. From our sensitization results, the zero vibrational level of $^4T_{2g}$ seems to be higher than the Michler's ketone triplet. However, the lack of sensitization by Michler's ketone could be due to the short lifetime of its triplet and/or to a low value of the energy-transfer rate constant caused by severe Franck–Condon restrictions.

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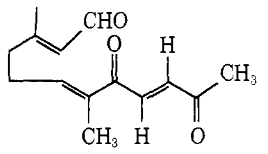
Cyclopentanoid Norsesquiterpenes from Gyrinid Beetles

Sir:

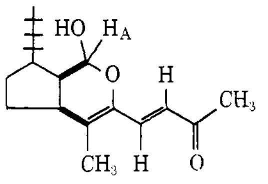
Although beetle secretions contain relatively simple compounds,[1] steroids and other more complex molecules have been identified recently.[2] The "whirl-a-gig" beetle (*Dineutes discolor* aubé, Coleoptera; *Gyrinidae*) secretes a complex mixture of C_{14} polycarbonyl compounds from its pygidial glands which have a defensive function toward fish.[3] Schildknecht and coworkers[4] and Meinwald and coworkers[5] have investigated four related species all of which contain an acyclic $C_{14}H_{18}O_3$ aldehyde (**1**) as the major component.

The major component of our secretion, gyrinidone (**2**), was separated from other glandular components and contaminants by extensive silicic acid column and thin layer chromatography.[6] It exhibited the following spectral properties: pmr ($CDCl_3$) δ 1.1 (d, J = 5.5 Hz, 4 H), 1.8 (narrow d, J < 1 Hz, 3 H), 2.3 (s, 3 H), 5.05 (d, J = 5.5 Hz, 1 H coupled to a proton at 1.78), 6.5 (d, J = 16 Hz, 1 H), 7.4 (d, J = 16 Hz, 1 H with seven additional protons between 1.1 and 2.3); ir 2.9, 5.98, 6.16, and 6.30 μ; uv (EtOH) 318 nm (ϵ 8700) and 234 (5600); mass spectra m/e 236.140 (33), 175 (22), 125 (58), 109 (50), 98 (68), and 43 (100). $C_{14}H_{20}O_3$ requires m/e 236.141. The appearance of hydroxyl absorption in the infrared spectrum was confirmed by formation of a monotrimethylsilyl ether having a molecular ion at m/e 308.[7] However, **2** formed a trimethoxime[8] (m/e 323) indicating that one oxygen functions either as carbonyl or hydroxyl.

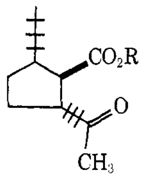
Oxidation of **2** with ruthenium tetroxide[9] gave only one acid (m/e 170) with large peaks at m/e 155, 152, 82, 81, and 43. Its methyl ester exhibited m/e 184, 169, 153, 152, 142, 129, 109, 100, and 43. The 2,4-dinitrophenylhydrazones of the epimerized[10a] acid and ester were identical with those of authentic[10b] **3a** and **3b**, which exhibit, respectively: **3a**, m/e 350, 315, 304, 297, 227; R_f 0.39 (benzene–ethyl acetate, 2:1); mp 170–173°; mmp 170–173° (lit.[10a] 170–172°); **3b**, m/e 364, 333, 329, 297, 246; R_f 0.50 (benzene–ethyl acetate, 10:1); elution at 270° on 1% OV-17 column on Supelcoport. Since the stereochemistry of **3a** from nepetalactone is known[10a] and the 2,4-DNP of our material exhibits the same sign of rotation and the same type curve as the authentic material, $[\alpha]^{25}{}_{578}$ −25° (c 0.04, C_2H_5OH), the sterochemistry of **2** is as shown.



1



2



3a, R = H
3b, R = CH_3

Isolation of **3a** from oxidation of **2** establishes the constitution of nine of the original 14 carbons in gyrinidone. The α,β-unsaturated ketone system in **2** constitutes four of the other five carbons as indicated by the absorption at δ 2.3, 6.5, and 7.4 in the pmr spectrum[11] and by the base peak at m/e 43 (CH_3CO^+) in the mass spectrum. The trans nature of the α and β protons is indicated by their large coupling constant (16 Hz). Since both protons appear as doublets, no other protons are adjacent to either. Their chemical shifts and the ultraviolet spectrum indicate an extended chain of conjugation which must be connected to the unsaturated methyl group in **2** (δ 1.8). The dual nature of one of the oxygens is accommodated by the hemiacetal linkage in **2**, the absorption at 5.05 being assigned to the proton H_A.[12,13]

The similarity of **2** to iridodial,[14] nepetolactone,[14] and plant iridoid glycosides[13] is striking. No cyclopentanoid norsesquiterpene has been found previously in nature.[15]

Three minor components of the secretion are isomeric $C_{14}H_{20}O_3$ compounds which contain a free aldehydic function indicated by a multiplet at δ 9.8. Prolonged contact (18 hr) with either silica gel or alumina isomer-

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