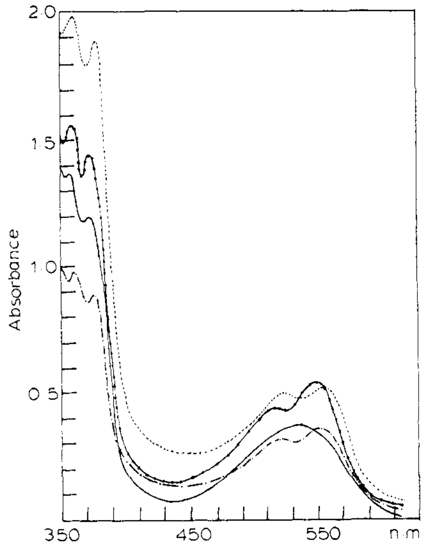

Figure 1. Absorption spectra for fluoradenide ions in methanol at 30°: (—) FD-KOMe (7.2×10^{-4} *M*, 0.143 *N*); (-·-·-·-) FD-Me_4NOMe (3.5×10^{-4} *M*, 0.045 *N*); (- - - -) FD-KOMe-18-crown-6 (2.9×10^{-4} *M*, 0.087 *N*, 0.462 *M*); (· - - · -) FD-Me_4NOMe-18-crown-6 (2.3×10^{-4} *M*, 0.077 *N*, 0.231 *M*) FD = fluoradene.

This spectrum is very similar to the spectra attributed to contact ion pairs of fluoradenide ion in THF and THP.[1] No detectable change in the spectrum was observed as [Me_4NOMe] was varied from 0.40 to 0.01 *M*.[3]

We also found that addition of 18-crown-6 to the potassium methoxide solutions produced an ion-pair spectrum. This spectrum showed maxima at 520 and 554 nm. The double maximum was still present when the concentration of potassium methoxide was made greater than that of crown ether but a gradual transition to a broad, single maximum was observed as the potassium methoxide concentration was increased. At high concentrations of potassium methoxide, the spectrum became indistinguishable from that observed in the absence of crown ether. Apparently the crown ether complexed ion pair and the species responsible for the broad maximum are sufficiently comparable in stability that the position of equilibrium can be driven toward the latter by increasing [KOMe]. Either of the following equilibria would explain this result

$$FD^-K^+CE + K^+ \rightleftharpoons FD^-K^+ + K^+CE$$
$$FD^-K^+CE + MeO^- \rightleftharpoons FD^- + MeO^-K^+CE$$

where FD^- = fluoradene anion, CE = crown ether, and methanol of solvation is omitted.

Both in this study and in the previous work, it has been found that no spectral changes occur as the concentration of alkali metal methoxide in methanol is changed (in the absence of crown ether). Moreover, both lithium and potassium methoxides produce the same spectrum. While we concede that these results suggest that the lithium, sodium, and potassium salts of fluoradene exist as free ions in methanol, we find it difficult to understand why a carbanion which exhibits a preference for ion pairing with tetramethylammonium ion and crown ether-complexed potassium ions would not also form ion pairs with methanol-solvated lithium, sodium, and potassium ions.

Ion pairing of alkali metal salts in methanol is marginal at the concentrations appropriate to conductance studies but can be observed.[4] It seems likely that most ion pairs are solvent separated in methanol[4b,5] and may be regarded as having the general formula $R^-M^+(MeOH)_n$. It is possible that this situation obtains for lithium, sodium, and potassium fluoradenides. If the number of methanol molecules was large, the cation and anion could be sufficiently insulated to render the spectral properties of the anion insensitive to the nature of the cation. It is interesting in this regard to note that addition of crown ether alters the tetramethylammonium ion pair and the new spectrum is identical with the crown ether-complexed potassium ion pair.

When nitrobenzene is added to solutions of fluoradenide ions in methanol, the fluoradenide ion is destroyed by a one-electron transfer process as evidenced by the precipitation of bifluoradene and by the appearance of nitrobenzenide ion (ESR). Interestingly, the rate of this process is much slower for solutions containing tetraalkylammonium or crown ether-complexed potassium ion pairs than for the uncomplexed potassium salt. When potassium methoxide is used to produce the fluoradenide ion, the rate increases markedly with increasing [KOMe] whereas it is independent of [Me_4NOMe] when this base is employed. The electron-transfer process is believed to be reversible and we are unprepared to present a detailed kinetic analysis at this time. It is clear, however, that the effective rate of the electron transfer process is quite sensitive to the type of ion pairs present. A similar effect had been reported[2f] for the reaction of 9-methoxyfluorene with nitrobenzene and methoxide salts. In that system the protonation rate of the carbanion was a factor in determining the overall rate. This complication can be disregarded in the case of fluoradene, because the anion concentration is directly monitored.

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(3) A referee has suggested that the observed spectrum might be due to an ion aggregate such as $FD^-M^+MeO^-$. We cannot rule out this possibility but the lack of spectral change over a wide range of concentrations makes it seem improbable. Either the spectral characteristics of the anion would have to be insensitive to aggregation changes or a particular state of aggregation would have to be favored over all others. It is worth mentioning that when [Me_4NOMe] was lowered to 0.0036 *M*, minor spectral changes were observed. Background absorption from the high fluoradene concentrations required prevented us from going to lower base concentration where we would expect to observe the free ion.

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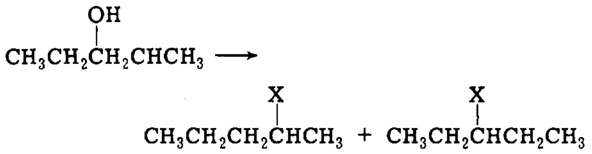
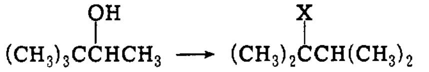
Conversions of Alcohols to Halides by Homolytic Reactions

Sir:

Preparation of alkyl halides from hindered or rearrangement-prone primary and secondary alcohols is difficult. Reagents such as HX, PX_3, PX_5, and SOX_2 often yield other products or halides resulting from hydride shifts[1] (eq 1) and alkyl rearrangements (eq 2).[2] Circumvention of the diffi-



$$CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}HCH_3 \longrightarrow CH_3CH_2CH_2\overset{X}{\overset{|}{C}}HCH_3 + CH_3CH_2\overset{X}{\overset{|}{C}}HCH_2CH_3 \quad (1)$$

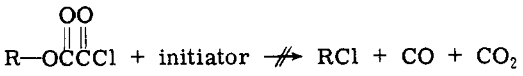


$$(CH_3)_3C\overset{OH}{\overset{|}{C}}HCH_3 \longrightarrow (CH_3)_2\overset{X}{\overset{|}{C}}CH(CH_3)_2 \quad (2)$$

culty with some secondary alcohols can be accomplished by conversion of the alcohol to tosylate and then reaction with halide ion.[1] Several reagents, e.g., $(C_6H_5)_3PBr_2$[3] and $(C_6H_5)_3P\text{-}CX_4$,[4] have been discovered which give clean reactions in somewhat sensitive systems.

In connection with other work, it was desired to convert 2,2-dimethylcyclohexanol to the corresponding halides. Using many of the usual reagents, including those mentioned above, known to bring about alcohol–halide transformations, in no instance was a detectable amount of the desired halide obtained. Reduction of 2,2-dimethylcyclohexanone by $LiAlH_4$ is very slow, and therefore it is not surprising that conversion of the alcohol to halide is difficult. These alcohol → halide reactions occur by heterolytic mechanisms (SN1 and SN2), and rearrangements and side reactions are sometimes difficult or impossible to control. Homolytic reactions would not be expected to exhibit these complications, and one can envision a number of groups in which homolysis of carbon–oxygen bonds occurs. Reaction of the alcohol with appropriate reagents could yield materials which undergo thermal or photolytic homolysis. Some reagents, in principle, could yield halides by free-radical chain reactions, e.g., ROCOCl and ROCOCOCl, and others by reaction of the alkyl radical intermediates with halogen donors, e.g., ROCS(OR) + $(R'O)_3P$ + CCl_4 or ROCOCOO-*t*-Bu + CCl_4. In this communication, the last-mentioned reaction is shown to convert very sensitive alcohols to halides in fair yields.

Attempts to convert alkyl chloroglyoxalates[5] to halides by radical chain reactions were unsuccessful. For example,

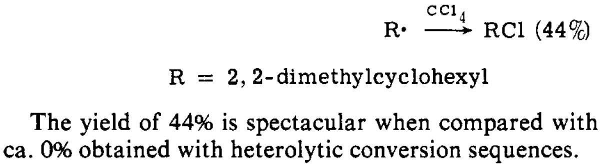


$$R{-}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl + \text{initiator} \not\longrightarrow RCl + CO + CO_2 \quad (3)$$

R = 2-methylcyclohexyl

thermal or photolytic (benzophenone sensitized) decomposition of catalytic amounts (~7 mol %) of benzoyl peroxide in the presence of 2-methylcyclohexyl chloroglyoxalate (eq 3) produced essentially no conversion of the glyoxalate and no detectable amount of the desired alkyl chloride.

Satisfactory yields of the desired products were obtained by decomposing 2,2-dimethylcyclohexyl *tert*-butylperoxyglyoxalate[6,7] in the presence of CCl_4, $BrCCl_3$, and similar halogen donors (eq 4).



$$ROH \longrightarrow RO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl \xrightarrow{t\text{-BuOOH}} RO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OO\text{-}t\text{-Bu} \xrightarrow[\text{warm}]{CCl_4}$$

$$R\cdot \xrightarrow{CCl_4} RCl\ (44\%) \quad (4)$$

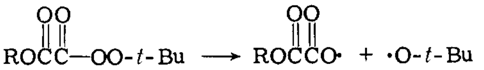
R = 2, 2-dimethylcyclohexyl

The yield of 44% is spectacular when compared with the ca. 0% obtained with heterolytic conversion sequences.

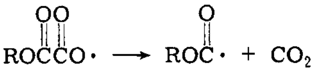
Table I. Preparation of Alkyl Halides by Thermolysis of Alkyl *tert*-Butylperoxyglyoxalates in Carbon Tetrahalide Solvents[a]

Starting alcohol	Halide[b]	% yield
Cyclohexanol	Cl	48
2,2-Dimethylcyclohexanol	Cl	44
3,3-Dimethyl-2-butanol	Cl	47
sec-Butyl alcohol	Cl	41
1-Octanol	Cl	28
tert-Butyl alcohol	Cl	59
Benzyl alcohol	Cl	~5
sec-Butyl alcohol	Br	25
1-Octanol	Br	~5

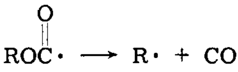
[a] Temp 95°; chlorides prepared in CCl_4, bromides in $BrCCl_3$ as solvent. [b] Corresponding to alcohol. In no instance was the presence of a rearranged halide observed in the NMR spectra of the crude reaction products or by GLC analysis. See text.



$$RO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}{-}OO\text{-}t\text{-Bu} \longrightarrow RO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}O\cdot + \cdot O\text{-}t\text{-Bu} \quad (5)$$



$$RO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}O\cdot \longrightarrow RO\overset{O}{\overset{\|}{C}}\cdot + CO_2 \quad (6)$$



$$RO\overset{O}{\overset{\|}{C}}\cdot \longrightarrow R\cdot + CO_2 \quad (7)$$

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3 \quad (8)$$

A reasonable mechanism for alkyl halide formation is shown in eq 5–8. Equations 5 and 6 and possibly 7 may be concerted if the resulting alkyl radical is especially stable. For the alkyl groups investigated, the yields vary in the order tertiary > secondary > primary and appear to be relatively insensitive to the hindrance at the carbon center undergoing reaction (Table I). Side products probably include carbonates, haloformates, and alkanes. Bartlett and coworkers[8] have shown that di-*tert*-butyl carbonate is obtained in 40% yield from the thermal decomposition of di-*tert*-butyl monoperoxyoxalate.

As is often found in free-radical reactions, the products are diverse and difficult to analyze. Fortunately no materials having GLC retention times similar to the desired products were observed. Rigorous analysis of the reaction products is underway, but thus far no rearranged halides have been observed. Except for the previously unreported 1-chloro-2,2-dimethylcyclohexane, commercial materials or compounds prepared by known procedures were obtained, and their NMR spectra and GLC retention times were identical with those of experimental products. Because 2-chloro-3,3-dimethylbutane and its most probable rearrangement companion, 2,3-dimethyl-2-chlorobutane, have the same retention time, the compound was collected, and its NMR spectrum was recorded. The observed spectral pattern, integration, and comparison with authentic rearranged material indicated the absence of the rearranged product to the extent detectable by these techniques.

It is anticipated that the procedure given herein and related reactions will prove to be valuable in preparing alkyl halides from alcohols. Also, most conversions of alcohols to other products proceed by heterolytic processes, and development of reaction schemes involving homolyses will probably, in many instances, be very worthwhile.

Alkyl Chloroglyoxalate. The alcohol (0.1 mol) was added dropwise over ca. 15 min into excess oxalyl chloride (0.2 mol) under nitrogen at 0°. When addition was complete, the ice bath was allowed to warm to room temperature (≈30 min) and was removed. A distillation column was attached, and the excess oxalyl chloride was removed by vacuum distillation. The product was then distilled, bottled, and kept in the dark.

Alkyl *tert*-Butylperoxyglyoxalate. Into a 25-ml round-bottomed flask under nitrogen were placed 0.0025 mol of *tert*-butyl hydroperoxide (>99% pure by iodometric titration), 0.0025 mol of pyridine, and 2.0 ml of CCl_4 (or CCl_3Br). The reaction flask was cooled in an ice bath, and a solution of 0.0025 mol of alkyl chloroglyoxalate in 3.0 ml of CCl_4 (or CCl_3Br) was added dropwise over a period of 10 min. Pyridine hydrochloride began precipitating immediately. When addition was complete, the ice bath was removed and the solution stirred for 15 min. The mixture was filtered into a 10-ml volumetric flask, and the reaction flask and precipitate were rinsed with CCl_4 (or CCl_3Br) which was added to the volumetric. An iodometric assay was run on the sample (which was theoretically 0.25 *M*) and generally showed the peroxide concentration to be 0.23–0.24 *M*.

Warning! Isolation of alkyl *tert*-butylperoxyglyoxalates is dangerous, and it is recommended that the compounds be prepared and reacted only in dilute solutions.

Decomposition of samples in sealed ampoules was carried out at 95° for 4, 6, and 9 min, and the reported yield is the average (which varied only 1–2%) determined by GLC.

Structures were assigned by comparison of retention times and NMR spectra with those of known materials. Assignment of structure to 2,2-dimethylcyclohexyl chloride was based on its NMR spectrum, principally the CHCl quartet at δ 3.7 which was reduced to a singlet upon irradiation of the signals at δ 1.2–2.0, and elemental analysis.

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Wavelength Dependence of the Photoionization of Phenolic Compounds

Sir:

Phenolic compounds are known to photodissociate with production of the characteristic phenoxyl radical.[1,2] In a flash photolysis study of neutral aqueous solutions of tyrosine, Feitelson and Hayon[3] showed that hydrated electrons are produced, supporting the photoionization mechanism

$$\begin{aligned} \mathrm{Ty\text{-}OH} &\rightarrow \mathrm{TyOH^+} + e^-_{aq} \\ \mathrm{TyOH^+} &\rightarrow \mathrm{TyO\cdot} + \mathrm{H^+} \end{aligned} \qquad \mathrm{(I)}$$

On the grounds of quenching experiments, they further proposed triplet tyrosine as a precursor of the reaction.[3,4]

Results obtained in our laboratory confirmed these views but showed a linear dependence of the yield of TyO· radical on the flash intensity, in contradiction with the quadratic law reported by Feitelson et al.[5] The flash duration and energy were quite comparable in both works (10 μsec; 1500–2000 J) but the spectral distributions of the flash lamps were not necessarily identical. We therefore investigated the intensity dependence of the photoionization yield for various spectral ranges of the exciting flash.

The following filter solutions were used: for excitation at $220 < \lambda < 360$ nm, $CoSO_4$ (240 g/l.) in water (this filter presents a low transmittance in the visible); for excitation at $\lambda > 270$ nm, carbon tetrachloride; for $240 < \lambda < 270$ nm, cyanine perchlorate[6] (0.4 g/l.) in water.

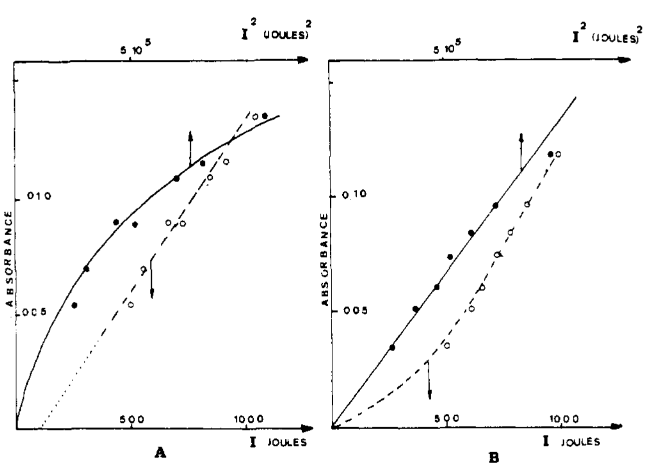

Figure 1. Absorbance of tyrosinyl radical as a function of the flash intensity: (A) excitation wavelengths, $240 < \lambda < 270$ nm; (B) excitation wavelengths, $\lambda > 270$ nm.

In each wavelength range, the flash output was proportional to the square of the applied voltage.

Upon flashing N_2 saturated solutions of tyrosine (2.5 10^{-4} mol/l.) at pH 6, the results were the following. (I) Suppression of most visible light did not appreciably affect the amount of [TyO] radical formed. (II) For an excitation restricted to the long wavelength side of tyrosine ($270 < \lambda < 300$ nm) a quadratic dependence of [TyO·] on the flash intensity is observed (Figure 1B). (III) Figure 1A shows that the tyrosine radical formation strongly deviates from a I^2 law for excitation wavelengths shorter than 270 nm. Due to experimental uncertainties and since the low intensity region cannot be explored in flash photolysis, it cannot be decided whether the linear plot in Figure 1A goes through the origin (in fact, the regression line does not).

Assuming triplet-triplet (TT) absorption to be responsible for the biphotonic ionization,[4] visible TT bands are seen to be inefficient in fluid solution. The quadratic law is obeyed only for $\lambda > 270$ nm. However, by monitoring the [OH·] adduct to tyrosine[3] formed upon conversion of e^-_{aq} by N_2O, we found a constant ratio: $[\mathrm{TyO\cdot}]/[e^-_{aq}]$. This result suggests that the same reaction (I) is operating following long or short wavelength excitation, eliminating in the latter case the possibility of a direct O–H bond rupture.

$$\mathrm{TyOH} \rightarrow \mathrm{TyO\cdot} + \mathrm{H\cdot} \qquad \mathrm{(II)}$$

Bent and Hayon[7] recently reported the TT absorption spectrum of tyrosine excited at 265 nm by a 15-nsec laser pulse. As an argument supporting the biphotonic mechanism, the authors mention that TyO· radicals are only formed during the exciting pulse. However, this observation does not exclude a one-photon ionization from a nonrelaxed singlet state. The existence of a true one-photon pathway at short wavelength, in addition to a biphotonic mechanism has been demonstrated for the β-bond cleavage of durene in a rigid matrix.[8] The fluorescence method allowed the investigation of the durene system at low light levels. In contrast to flash photolysis experiments the formation of bityrosine has been studied at low excitation rates by monitoring its fluorescence. Shimizu[9] concludes to a monophotonic process, in the case of an excitation at 275 nm. However, his work refers to air-saturated solutions and the conclusion should be applied with caution to our case since oxygen might be implied in a direct reaction with the tyrosine triplet state.[5]