Photo-promoted Oxidation of Alcohols with Aliphatic *N*-Chloroamines

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Irradiation of *NN*-dichloro-t-butylamine (1) with alcohols, especially alcohols of benzylic type, in CCl_4 was found to give the corresponding ketones and aldehydes with quantitative formation of t-butylamine hydrochloride. The photoreaction of 1-phenylethanol with (1) in cyclohexane or toluene, however, gives mainly solvent-chlorinated products together with a low yield of acetophenone. The oxidation is suppressed by HCl scavengers (triethylamine or epichlorohydrin) and accelerated by the addition of HCl irrespective of irradiation. The irradiation may induce generation of Cl· and then HCl, the latter exerting autocatalysis for the oxidation in the dark. An ionic mechanism *via* protonated (1) and alkyl hypochlorite is postulated and discussed.

As reviewed by some workers,[1-3] *N*-chloroamines have mainly been used for amination and/or chlorination of various hydrocarbons. In contrast to *N*-halogeno-amides and -imides,[4,5] *N*-chloroamines have hardly been used as oxidants except for NH_2Cl which oxidises benzyl alcohol or benzylamine to benzaldehyde and also aniline to azobenzene.[6] Our previous studies [7,8] on photo-promoted oxidation involving *N*-chloroamino-compounds led us to examine the possibility of oxidising alcohols with *N*-chloroamines.

It was found that irradiation of *NN*-dichloro-t-butylamine (1) in CCl_4 effected oxidation of alcohols. Specifically, the photo-oxidation with (1) was examined in some solvents and also in the presence of HCl or scavengers of HCl.

RESULTS AND DISCUSSION

A number of *N*-chloroamines were used to oxidise cyclohexanol in the dark. Monochloroamines such as *N*-chlorodimethylamine did not react under reflux in CCl_4 for several hours, and dichloroamines such as *NN*-dichloro-t-butylamine often decomposed to the corresponding amine hydrochloride after 1—7 days at room temperature, affording cyclohexanone (10—20%). Since *NN*-dichloro-t-butylamine (1) can be purified,† it was selected as an oxidant.

Photoreaction of alcohols with Bu^tNCl_2 (1) in CCl_4 [a]

Alcohol	Mol of (1)	Alcohol consumed (%)	Product	Yield [c] (%)	Yield of Bu^tNH_3Cl (%)
Cyclohexanol	0.50	56	Cyclohexanone	23	86
	1.00	90		17	90
$PhCH_2OH$	0.79	85	PhCHO	20	82
$PhCH(OH)CH_3$	0.43	73	$PhCOCH_3$	67	88
	0.43	76		65	91
	0.85	100		74	91
	0.85 [b]	100		75	92
p-$ClC_6H_4CH(OH)CH_3$	0.79	92	p-$ClC_6H_4COCH_3$	78	80
Ph_2CHOH	0.40	100	$Ph_2C{=}O$	98	90
	0.79	100		84	86

[a] Irradiation with >290 nm light at 20 °C, unless otherwise noted. [b] Thermal reaction induced by benzoyl peroxide at 80 °C. Based on alcohol consumed.

Since (1) has $\lambda_{max.}$ at 310 nm, irradiation (>290 nm) of (1) and alcohols in CCl_4 initiated the reaction which did not start in the dark. t-Butylamine hydrochloride was separated rapidly ‡ and carbonyl compounds were identified (Table).

The yields of aldehydes from aliphatic primary alcohols were low and those of ketones from secondary alcohols were below 40% based on alcohol consumed, whereas those from benzylic alcohols were higher in the order of $PhCH_2OH < PhCH(OH)Me < Ph_2CHOH$. The Table also shows that the thermal reaction induced by benzoyl peroxide results in a similar yield (*e.g.* from 1-phenylethanol). As described below [equation (1)], photo-acceleration may be due to N–Cl bond fission leading to generation of HCl as in the reactions of chloroamines and *N*-chloroamino-acids.[7,8] Benzoyl peroxide with (1) generates HCl probably *via* formation of an alcohol radical which can donate a hydrogen atom to (1).

The photoreaction of (1) and 1-phenylethanol in cyclohexane or toluene gave predominantly chlorocyclohexane (68%) and benzyl chloride (51%), respectively, with lower yields of acetophenone and t-butylamine hydrochloride.§ This suggests the generation of chlorine atom and *N*-chloro-t-butylaminyl radical.

In the oxidation of 1-phenylethanol with (1), addition of amine (Et_3N) or epoxide (epichlorohydrin) decreased the yield of ketone against our expectation that these HCl scavengers may accelerate the oxidation by analogy with the case of Bu^tOCl.[10] In contrast, the addition of HCl

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† Preparative experiments suggested that *N*-chloroamines possessing neither amine hydrogen nor alkyl α-hydrogen are stable, which may be due to inhibition of imine formation.[9]

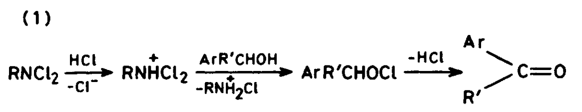
‡ Quantum yield for the oxidation of 1-phenylethanol with (1) in CCl_4 was *ca.* 5 based on the actinometry by benzophenone–diphenylmethanol in benzene.

§ Reaction in acetonitrile gave the same products as in CCl_4.

accelerated the reaction under both dark and irradiated conditions. For example, addition of Et_3N (5 mmol) to a mixture of $PhCH(OH)CH_3$ (10 mmol) and Bu^tNCl_2 (5 mmol) gave only 4% yield of $PhCOCH_3$ under irradiation, while addition of HCl to the same system gave 63% yield of the ketone even in the dark.

Hydrogen chloride, which is produced from Cl· at the initial stage by irradiation or addition of a radical source, may act as an autocatalyst for ketone formation. Molecular chlorine was generated on treatment of (1) with HCl by analogy with the formation of BrCl from *N*-bromosuccinimide and HCl[11] in the dark, but it was observed that molecular chlorine could not oxidise alcohols under these conditions. Hence a tentative mechanism for the oxidation may be expressed as equation (2), which assumes an intermediate alkyl hypochlorite (3) as postulated for the bromine oxidation of phenylbenzoins[12] and mandelic acid.[13]

$$\underset{(1)}{\mathrm{RNCl_2}}\left(\xrightarrow[-\mathrm{R\dot{N}Cl}]{h\nu}\mathrm{Cl\cdot}\right)\xrightarrow{\text{H-sources}}\mathrm{HCl} \qquad (1)$$



$$\underset{(1)}{\mathrm{RNCl_2}}\xrightarrow[-\mathrm{Cl^-}]{\mathrm{HCl}}\underset{(2)}{\mathrm{R\overset{+}{N}HCl_2}}\xrightarrow[-\mathrm{R\overset{+}{N}H_2Cl}]{\mathrm{ArR'CHOH}}\underset{(3)}{\mathrm{ArR'CHOCl}}\xrightarrow{-\mathrm{HCl}}\mathrm{\overset{Ar}{\underset{R'}{>}}C{=}O} \qquad (2)$$

(1) (2) (3)

The conversion of ArR'CHOH into ArR'C=O by hydrogen abstraction with Cl· atom is less important in view of our observations of (a) a very poor yield of acetophenone from an irradiated mixture of 1-phenylethanol and Cl_2 (*i.e.* Cl·) in spite of the reported generation of radical species from $R\overset{+}{N}HCl_2$,[14,15] and (b) virtually no formation of chlorocyclohexane from a mixture of (2) and cyclohexane in the dark. The yield of carbonyl compound was not affected by the displacement of O_2 by N_2, which also supports the ionic mechanism.

The observed increase of yields of ketones by the substitution of an α-aryl group can be ascribed to the acceleration of dehydrochlorination of hypochlorite (3) due to the delocalization of the developing negative charge at the α-carbon.

t-Butylamine hydrochloride was formed quantitatively regardless of alcohols (Table) and also on irradiation of (1) alone. The salt was easily formed, when *N*-chloro-t-butylamine (4) alone was kept standing in the dark and under irradiation.

Irradiation of (4) and 1-phenylethanol in molar ratio 2 : 1 in CCl_4 gave $R\overset{+}{N}H_3Cl^-$ quantitatively together with only 3% yield of acetophenone (>90% recovery of alcohol) (*cf.* Table). The lower oxidation ability of (4) may be ascribed to the poorer ability of (4) to generate Cl^+ at the transition state[1] for the formation of hypochlorite (3).

EXPERIMENTAL

Materials.—*NN*-Dichloro-t-butylamine (1)[16] was prepared by the reaction of t-butylamine with HOCl in the presence of a large excess of $NaHCO_3$. The purity of (1) was checked by iodometry, δ (CCl_4) 1.37, $\lambda_{max.}$ (CCl_4) 310 nm (ε 405) (lit.,[17] 312 nm), (EtOH) 309 nm (ε 298). *N*-Chloro-t-butylamine (4) was prepared from t-butylamine and NaOCl.[18] To an aqueous solution of NaOCl (61 mmol) was added t-butylamine (4.2 g, 60 mmol) with stirring. After a few minutes, the resulting upper layer was separated and dried (Na_2SO_4) to give (4), δ (CCl_4) 1.19 (9 H, s), 4.0br (1 H, s), $\lambda_{max.}$ (hexane) 260 nm (ε 400), (CH_3CN) 258 nm (ε 416). This chloroamine decomposes on standing at room temperature. The following *N*-chloroamines were prepared for reaction with cyclohexanol: *N*-chlorodimethylamine, δ (CCl_4) 2.88; *N*-chlorodiethylamine, δ 1.20 (3 H, t, *J* 7 Hz) and 2.91 (2 H, q, *J* 7 Hz); *N*-chloromorpholine, δ 3.15 (4 H, m) and 3.71 (4 H, m); *NN*-dichlorohexylamine, δ 0.8—2.1 (m), 0.92br (t), and 3.65 (2 H, t). 1-(4-Chlorophenyl)ethanol was obtained by reduction of the corresponding ketone with sodium borohydride, b.p. 75—76 °C at 0.6 mmHg (lit.,[19] 81—86 °C at 1 mmHg), δ (CCl_4) 1.28 (3 H, d, *J* 6 Hz), 3.43 (1 H, d, *J* 4 Hz, OH), 4.60 (1 H, qd, *J* 6 and 4 Hz, CH), and 7.15 (4 H, s, derived from A_2B_2). On addition of D_2O, the signal due to OH disappeared and the methine proton became a quartet. The other alcohols and ketones used were commercially obtained.

Instruments.—G.l.c. analyses were carried out on a Yanaco G 180 using a column packed with PEG 20M or Silicone SE30. Irradiation was conducted on a merry-go-round apparatus equipped with a Halos 300 W high-pressure mercury lamp. U.v. and n.m.r. spectra were recorded on a Hitachi 124 spectrophotometer and R 24 B model, respectively.

Reaction of NN-*Dichloro-t-butylamine* (1) *with Alcohols.*—A solution of the alcohol (10.0 mmol) and (1) in CCl_4 (20 ml) was irradiated at *ca.* 20 °C until the disappearance of (1) (1—1.5 h) was shown by iodometry. The solid separated was filtered, washed with CCl_4, and dried to give >95% pure t-butylamine hydrochloride. The filtrate combined with the washings was analysed by g.l.c. after addition of biphenyl or some other g.l.c. standard (Table). In the case of 1-phenylethanol, the same reaction mixture to which 0.5 mmol of benzoyl peroxide was added was heated under reflux for 1 h, and worked up similarly.

Reaction of 1-*Phenylethanol with* NN-*Dichloro-t-butylamine* (1) *in the Presence of Organic Solvents.*—A solution of 1-phenylethanol (10.0 mmol) and (1) (7.9 mmol) in CCl_4, cyclohexane, toluene, or acetonitrile (20 ml) was irradiated for 1 h. Yields of chlorocyclohexane and benzyl chloride were calculated on the basis of (1).

Reaction of 1-*Phenylethanol with* N-*Chloro-t-butylamine* (4).—A solution of 1-phenylethanol (10.0 mmol) and (4) (18 mmol) in CCl_4 (20 ml) was irradiated for 2.5 h. t-Butylamine hydrochloride [86% based on (4)] was isolated. The other components of the products were unchanged alcohol (90%) and acetophenone (3%).

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