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THE DECOMPOSITION OF SOME TERTIARY ACYL HYPOCHLORITES

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In recent years the photochemical and thermal decomposition of tertiary hypochlorites have received much attention and their free radical chain mechanism elucidated[2,3]. These compounds undergo decomposition to carbonyl compounds and alkyl chlorides. The structure of the products appears to depend upon the nature of the R groups and their subsequent stability as a free radical which is generated in the β-scission process.

$$R_1RRCOCl \longrightarrow RRCO + R_1Cl$$

We have set out to study a series of tertiary α-acylhypochlorites in hopes of finding a new method for generating the acyl radical and establishing its order of stability with various alkyl radicals.

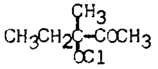
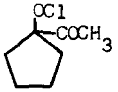
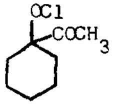
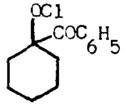
$$R_1RRCOCl \longrightarrow R_1COCl + RCOR$$

We, at this time, would like to report our preliminary findings on five of these.

Each hypochlorite was prepared by treatment of the corresponding tertiary ketols with hypochlorous acid in carbon tetrachloride[3]. The solutions were then assayed iodometrically and refluxed in the dark from 5 to 30 minutes at which time all the hypochlorite had decomposed.

TABLE 1

Decomposition of Tertiary Acyl Hypochlorites in Refluxing CCl_4

Hypochlorite	Products[a]	Yield %
(1)  $CH_3CH_2\underset{OCl}{\overset{CH_3}{C}}-COCH_3$	2-butanone; acetyl chloride	99^b
(2) $(CH_3)_2COClCOC_6H_5$	benzoyl chloride; acetone	95^c
(3) 	cyclopentanone; acetyl chloride	90
	$ClCH_2(CH_2)_3COCOCH_3$	$<6^d$
(4) 	cyclohexanone; acetyl chloride	46^e
	2-chlorocyclohexanone	44^e
(5) 	cyclohexanone; benzoyl chloride	42^e
	2-chlorocyclohexanone	48^e
	$ClCH_2(CH_2)_4COCOC_6H_5$	$<5^d$

[a] Identity of all products established by retention times in the gas chromatograph and by infrared analysis.

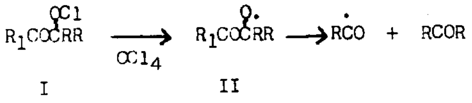
[b] No other products indicated by gas chromatography.

[c] Identified as benzoic acid after hydrolysis.

[d] Unidentified high boiling peak.

[e] Yield established by gas chromatography using the internal standard method[4].

The proposed mechanism for this reaction is analogous to that suggested by Walling and Greene in their studies of the fragmentation of tertiary hypochlorites[2,3].



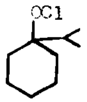
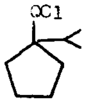
$$\underset{I}{R_1CO\overset{OCl}{C}RR} \xrightarrow[CCl_4]{} \underset{II}{R_1CO\overset{O\cdot}{C}RR} \longrightarrow R\dot{C}O + RCOR$$

$$R\dot{C}O + I \longrightarrow RCOCl + II$$

It is of interest to compare the products of compounds (3), (4) and (5) in Table I with Greene's results with the hypochlorites of isopropyl cyclohexanol and isopropyl cyclopenanol[3]. Although we have not been able to identify any ring opening products it is fair to say our system seems more favorably disposed toward acyl cleavage rather than alkyl cleavage and the amount of 2-chlorinated cyclic ketone in our case is much higher. This selectivity in the mode of cleavage indicates a new and potentially useful method of generating acyl radicals.

TABLE 2[3]

Products of Decomposition of Tertiary Hypochlorites

Hypochlorite	Solvent	Products	Yield %
	CCl_4[a]	isopropyl chloride; cyclohexanone	66
		$(CH_3)_2CHCO(CH_2)_4CH_2Cl$	13.5
		2-chlorocyclohexanone	<0.5[b]
	$CFCl_3$[c]	$(CH_3)_2CHCO(CH_2)_3CH_2Cl$	94
		isopropyl chloride; cyclopentanone	3.4

[a] Thermal initiation at 80°.

[b] Not present within the limits of detection of the analysis.

[c] Weak ultraviolet initiation at 0°.

Acyl radicals have been shown to be intermediates in vapor phase decompositions of some ketones and aldehydes and are usually generated in solution by peroxides or photochemically[5]. They have also been shown to be intermediates in the cobaltic salt oxidations of aldehydes[6]. The photolysis of xanthates[7] and the reaction of tri-alkyltin hydrides with acid chlorides[8] represent other and more recently reported methods of producing the acyl radical.

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