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OXYGENOLYSIS OF KENTENIMINES IN THE PRESENCE OF COPPER(II) CHLORIDE

Marvin W. Barker* and Subramoniam I. Perumal
Department of Chemistry, Mississippi State University
Mississippi State, MS. 39762 USA

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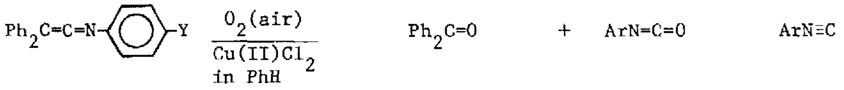
The increasing attention that metal ion-catalyzed oxygenations have been receiving prompted us to investigate the effect this process would have on the heterocumulene ketenimine. Three prior studies on the oxygenation of ketenimines have been reported. The first report was by Staudinger and Hauser who observed that ketenimines were oxygenated by air at elevated temperatures[1]. The only products observed were ketones and isocyanates, and a dioxetane intermediate was proposed to account for the products. More recently Kagen and Lillien[2] and Crandall and Crawley[3] have investigated the peroxyacid oxygenation of ketenimines, and each group proposed an epoxide intermediate to account for the observed production of ketones, isonitriles and α-acyloxyamides (no isocyanate was observed). Crandall and Crawley also employed an epoxide intermediate to explain the ketones and isonitriles produced when ketenimines are treated with ozone[3].

We have observed that aryl substituted ketenimines undergo a rapid reaction with oxygen (air) at room temperature if copper(II) chloride is present in the reaction mixture. Without the copper(II) chloride no oxygenation is observed under these conditions. The products of this catalyzed oxygenation, unlike the earlier studies, are ketones, isocyanates, and isonitriles, (Eq.1). The following is typical of a preparative run: A stream of dry air was passed through a solution of diphenyl-N-phenylketenimine (0.02M) in 200 ml of anhydrous benzene to which 0.005 mole of copper(II) chloride had been added. The reaction was monitored by the ketenimine absorption in the IR at 2000 cm^{-1}. Disappearance of this peak was complete in 3.5 hours. The reaction mixture was filtered, concentrated to 50 ml, and analyzed for benzophenone and for phenyl isocyanate by glc. (An internal standard was added for calibration purposes). Removal of the remaining benzene under reduced pressure and the leaching of the resulting residue with ether to remove the benzophenone and phenylisocyanate left the copper complex of phenyl isonitrile[4]. Yields for this run and for several other ketenimines are found in the Table. (Control reactions were performed to prove that isocyanate was not arising from the oxidation of isonitrile.)

From Eq. 1, one observes that one equivalent of ketone should be obtained from each equivalent of ketenimine while the total of the equivalents of isonitrile and isocyanate should be one for each equivalent of ketenimine. Obviously the isonitrile plus isoncyanate value is low. This appears to be due mainly to the low yield of isonitrile, a result found in the peroxyacid oxygenation of ketenimines studies[2,3]. One reason is probably the propensity of this group to polymerize under these conditions . If the assumption is made that the yields of benzophenone correspond

TABLE

OXYGENATION OF KETENIMINES



Eq. 1

Y	$Ph_2C=O$ %	$ArN=C=O$ %	$ArN\equiv C$ %	% Yield Benzophenone / % Yield Isocyanate
OCH_3	60.2	40.1	0.6	1.5
CH_3	54.9	16.8	2.2	3.3
H	81.1	20.1	1.2	4.0
Br	82.9	17.1	2.5	4.8
Cl	63.1	9.2	1.3	6.9
F	95.0	10.1	1.7	9.4

to yields for the overall reaction, then the ratio of the yields of benzophenone to isocyanate should indicate the relative amount of isocyanate produced from each ketenimine (TABLE). Also any variation in the amount of isocyanate produced would indicate an inverse variation in the amount of isonitrile produced. The data in TABLE show that the amount of benzophenone to isocyanate increases sharply with increasing electron withdrawing power of Y. This would indicate that the amount of isocyanate produced by the oxygenolysis decreases with increasing electron withdrawing power of Y, and, therefore, the amount of isonitrile actually produced increases with increasing electron withdrawing power of Y. Thus, in this particular oxygenation of ketenimines, the nature of Y strongly effects the products obtained. This observation has not been previously reported.

Although the heterocyclic intermediates first proposed by Staudinger and Hauser[1] and by Kagen and Lillien[2] may be responsible for the products observed in this copper (II) chloride catalyzed oxygenation, alternate pathways may be possible. For instance, copper(II) catalyzed oxygenations of amines are reported to occur through a cation-radical[5]. This cation-radical is stabilized by electron donating substituents and destabilized by electron withdrawing substituents. The ratio of isocyanate to isonitrile we are observing which results from a similar change in electron withdrawing character of the ketenimine N-aryl substituent suggests a cation-radical intermediate could be involved in this oxygenation. To check this possibility, we performed the oxygenation in acetonitrile and in 1,2-dimethoxyethane. The reaction proved much faster in these more polar solvents. We are testing this hypothesis further with kinetics and ESR studies.

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