The Copper-promoted Oxidation of Tri-n-butylamine. The Carbon-by-Carbon Degradation of an n-Butyl Group

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Summary The copper(I) chloride-promoted oxygenation of tri-n-butylamine at 80° yields di-n-butylamine, *NN*-di-n-butylformamide, *NN*-di-n-butylacetamide, *NN*-di-n-butylpropionamide, *NN*-di-n-butylbutyramide, and tetra-n-butyloxamide.

THE reaction of tri-n-butylamine with copper(I) chloride (2·7 : 1 molar ratio) and oxygen in refluxing benzene results in a mixture of *NN*-di-n-butylamides and di-n-butylamine. These products and unreacted starting amine are listed in the Table along with their yields as determined by g.l.c. Two features are apparent: one of the butyl groups has been removed in a manner that appears to have involved the loss of one carbon atom at a time and *NN*-di-n-butylformamide and *NN*-di-n-butylpropionamide are the major products (combined yield *ca.* 41%).

Products[a]	Yields (%)	
Di-n-butylamine	7·0[b]	3·1[c]
Tri-n-butylamine	23·3	27·1
NN-Di-n-butylformamide	9·4	9·4
NN-Di-n-butylacetamide	4·1	4·4
NN-Di-n-butylpropionamide	31·7	33·1
NN-Di-n-butylbutyramide	2·0	2·0
Tetra-n-butyloxamide	*ca.* 2·0	trace

[a] Isolated by trapping and identified by comparison of their i.r. spectra with authentic materials.
[b] 10 hr. [c] 17 hr.

Tri-n-butylamine has been oxidized by manganese dioxide,[1] ozone,[2] neutral permanganate,[3] and nitric acid.[4] In all these instances, the products have been *NN*-di-n-butylformamide, *NN*-di-n-butylbutyramide, and di-n-butylamine, the first compound being the major product. The solvent in the nitric acid oxidation,[4] acetic anhydride, reacted with the di-n-butylamine produced to give *NN*-di-n-butylacetamide. The oxidation reported here is unusual in that *NN*-di-n-butylacetamide and *NN*-di-n-butylpropionamide are formed from the starting amine and that the propionamide is the major product of the reaction.

In the oxidations already referenced,[1–4] the intermediate is considered to be the enamine, 1-di-n-butylaminobut-1-ene (**1**). In fact, when the ozone oxidation was carried out at

$$(CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2)_2{\cdot}NCH:CH{\cdot}CH_2{\cdot}CH_3 \quad (\mathbf{1})$$

−78°, a 34% yield of (1) was obtained.[2] In a more pertinent case, the copper(I) chloride complex with triethylamine at 0° generated acetaldehyde and diethylamine when water was added.[5] These are the hydrolysis products of diethylvinylamine.

The reaction of (**1**) with copper(I) chloride and oxygen was run under the same conditions as for tri-n-butylamine. Analysis of the crude reaction mixture by g.l.c. indicated that di-n-butylamine was the major product which was probably produced by hydrolysis. All the amides listed in the Table were also detected. However, now *NN*-di-n-butylformamide was the major product among the amides and *NN*-di-n-butylpropionamide, although present, was there at about the same concentration as the acetamide and butyramide.

We feel that these results implicate the formation of the enamine (**1**) in the copper(I) chloride–oxygen reaction with tri-n-butylamine. Oxidative cleavage of the enamine would give *NN*-di-n-butylformamide and propanal, and hydrolysis of the enamine would give di-n-butylamine and butanal. Both of these aldehydes were detected in the ozone oxidation of tri-n-butylamine,[2] but our method of work-up precluded their isolation. Further reaction of these two aldehydes with di-n-butylamine to give the carbinolamines ($R^1 = Et$ and Pr, equation 1) and subsequent reaction with the oxidant would give *NN*-di-n-butylpropionamide ($R^1 = Et$), and *NN*-di-n-butylbutyramide ($R^1 = Pr$). The oxidation of the intermediate

$$Bu^n{}_2NH + R^1CHO \rightarrow Bu^n{}_2NCHR^1OH \xrightarrow[O_2]{CuCl} Bu^n{}_2NCO{\cdot}R^1 \quad (1)$$

carbinolamine ($R^1 = Pr$), was suggested as the source of *NN*-di-n-butylbutyramide.[2,3] Elimination of water from the carbinolamines would give the enamines ($R^2 =$ Me and $R^2 = Et$ (equation 2), which can be further oxidized. Oxidation of the enamine, $R^2 = Me$, would

$$Bu^n{}_2CHR^1OH \longrightarrow Bu^n{}_2NCH{=}CHR^2 + H_2O \qquad (2)$$

give *NN*-di-n-butylformamide and acetaldehyde. Further reaction of acetaldehyde with di-n-butylamine (equation 1, $R^1 = Me$) would eventually give *NN*-di-n-butylacetamide.

The formation of tetra-n-butyloxamide is most easily explained by the dimerization of two di-n-butylaminoformyl radicals generated by oxidation of the *NN*-di-n-butylformamide produced in the reaction. This appeared likely, since dialkylformamides can be converted into oxamides in good yield with peroxides.[6] However, an attempt to oxidize *NN*-di-n-butylformamide with the copper(I) chloride–triethylamine complex and oxygen at 80° failed to give any detectable amount of oxamide.

The fact that *NN*-di-n-butylpropionamide is the major product of the reaction cannot be explained by the sequence of reactions already offered. Rather, *NN*-di-n-butylformamide should be the major amide as was found when the enamine (**1**) was oxidized. A possible explanation for the high yield of propionamide is that a skeletal rearrangement occurs in some step prior to enamine formation which eventually leads to the isomeric enamine (**2**). Oxidative cleavage of (**2**) should lead to *NN*-di-n-butylpropionamide. Such a rearrangement of a nitrogen from one carbon to an

$$Bu^n{}_2N{\cdot}CEt{:}CH_2 \qquad (\mathbf{2})$$

adjacent one has precedent in the Neber rearrangement[7] and the rearrangement of an amine to an α-amino-ketone.[8]

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