

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

By R. A. JERUSSI* and M. R. McCORMICK

(General Electric Research and Development Center, Schenectady, New York, 12301)

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*	Yields (%)	
Di-n-butylamine	7.0 ^b	3.1 ^c
Tri-n-butylamine	23.3	27.1
<i>NN</i> -Di-n-butylformamide	9.4	9.4
<i>NN</i> -Di-n-butylacetamide	4.1	4.4
<i>NN</i> -Di-n-butylpropionamide	31.7	33.1
<i>NN</i> -Di-n-butylbutyramide	2.0	2.0
Tetra-n-butyloxamide	<i>ca.</i> 2.0	trace

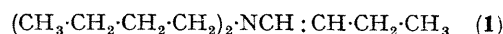
* Isolated by trapping and identified by comparison of their i.r. spectra with authentic materials.

^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

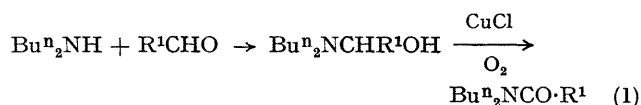
is considered to be the enamine, 1-di-n-butylaminobut-1-ene (**1**). In fact, when the ozone oxidation was carried out at



–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 ($\text{R}^1 = \text{Et}$ and Pr , equation 1) and subsequent reaction with the oxidant would give *NN*-di-n-butylpropionamide ($\text{R}^1 = \text{Et}$), and *NN*-di-n-butylbutyramide ($\text{R}^1 = \text{Pr}$). The oxidation of the intermediate



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

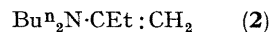
oxidized. Oxidation of the enamine, $R^2 = \text{Me}$, would



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

The formation of tetra-*n*-butyloxamide is most easily explained by the dimerization of two di-*n*-butylamino-formyl 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



adjacent one has precedent in the Neber rearrangement⁷ and the rearrangement of an amine to an α -amino-ketone.⁸

(Received, April 14th, 1969; Com. 505.)

¹ H. B. Henbest and M. J. W. Stratford, *J. Chem. Soc. (C)*, 1966, 995.

² H. B. Henbest and M. J. W. Stratford, *J. Chem. Soc.*, 1964, 711.

³ H. Schechter and S. S. Rawalay, *J. Amer. Chem. Soc.*, 1964, **86**, 1706.

⁴ Y. Ogata, Y. Sawaki, and Y. Kuriyama, *Tetrahedron*, 1968, **24**, 3425.

⁵ J. F. Weiss, G. Tollin, and J. T. Yoke, *Inorg. Chem.*, 1964, **3**, 1344.

⁶ L. Freidman and H. Shechter, *Tetrahedron Letters*, 1961, 238.

⁷ P. W. Neber and G. Huh, *Annalen*, 1934, **515**, 283.

⁸ H. E. Baumgarten and J. E. Petersen, *J. Amer. Chem. Soc.*, 1960, **82**, 459.