micro boiling point at atmospheric pressure gave a value of 190.5-191° (lit.[14] 189-191°).

5-Bromo-*m*-Xylene.—This compound was prepared by the method of Buehler, *et al.*,[15] in 27.6% yield, bp 33° (0.1 mm) [lit.[15] bp 70° (6 mm)].

Reaction of Diphenyl-*p*-Tolylsulfonium Bromide with Sodium *t*-Butoxide.—A sample of 0.357 g (0.001 mol) of diphenyl-*p*-tolylsulfonium bromide was mixed with 6 ml of an approximately 0.16 *M* (1 equiv) slurry of sodium *t*-butoxide in anhydrous *t*-butyl alcohol, and the mixture was refluxed under an efficient condenser for 24 hr. During this time a precipitate of sodium bromide formed. The reaction mixture was then subjected to vpc analysis. Quantitative determinations were carried out by use of an F & M Model 609 gas chromatograph equipped with a 2-ft Apiezon L column; a time–temperature program from 25 to 200° at 4.6°/min was employed. Standards were prepared as in the analyses of the pyrolysates, and the product percentages were determined graphically. Quantities of the unknown materials were estimated by measurement of their peak areas. The results of this analysis are listed in Table III.

Trace amounts of materials in the reaction mixture were identified by use of an Aerograph Autoprep Model A-700 gas chromatograph equipped with a 20-ft silicone rubber column. The minor products were identified by retention times. Where possible, a small amount of an authentic sample of the suspected material was added to a small quantity of the mixture and an increase in peak height was observed. An attempt was made to collect a sample of the unknown ether by preparative gas chromatography, the Autoprep being used. A very small amount of the material was collected and subjected to nmr analysis. A carbon tetrachloride solution of the substance gave a weak signal; however, the presence of *t*-butyl and aromatic methyl groups was indicated. The retention time was about that expected for a tolyl or xylyl *t*-butyl ether other than *t*-butyl *p*-tolyl ether, and the substance had the odor of an ether.

Although both were formed in small amounts, it was possible to see that toluene was formed in greater quantity than benzene. The presence of a polymeric material was also indicated by a very broad "peak" which was observed at long retention times.

Registry No.—Phenyl-*p*-tolyl-2,4-dimethylphenylsulfonium iodide, 16720-21-1; phenyl-*p*-tolyl-2,4-dimethylphenylsulfonium bromide, 4063-74-5; phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium chloride, 4063-73-4; *p*-tolyl 2,5-dimethylphenyl sulfide, 16704-44-2; phenyl 2,5-dimethylphenyl sulfide, 16704-45-3; *p*-tolyl 2,4-dimethylphenyl sulfide, 16704-46-4; phenyl 2,4-dimethylphenyl sulfide, 16704-47-5; *p*-tolyl 2,5-dimethylphenyl sulfoxide, 16704-48-6; phenyl 2,5-dimethylphenyl sulfoxide, 16704-49-7.

Acknowledgments.—This work was supported by Grant GP 182 from the National Science Foundation. One of us (G. H. W.) also gratefully acknowledges support as a National Science Foundation Cooperative Graduate Fellow. The Varian A-60 nmr apparatus used in this work was purchased with funds donated to the University of Massachusetts by the National Science Foundation.

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[14] J. Pinette, *Ann.*, **243**, 32 (1888).

[15] C. A. Buehler, T. A. Magee, K. V. Nyak, and D. M. Glenn, *J. Org. Chem.*, **24**, 1307 (1959).

Ozonation of Amines. II. The Competition between Amine Oxide Formation and Side-Chain Oxidation

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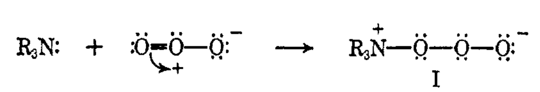
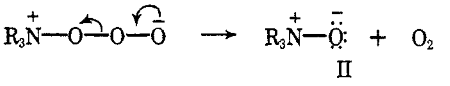
The competition between amine oxide formation and side-chain oxidation during ozonation of tri-*n*-butylamine in several different solvents has been studied, using ozone–nitrogen mixtures. To obtain a better understanding of the side-chain oxidation, 1-di-*n*-butylamino-2-butanone (XV) was synthesized and ozonized. A preference for attack at the methylene group between the amino and carbonyl groups was observed. The results, including solvent effects, are explained on the basis of competitive fates of an initial amine–ozone adduct.

In the first paper of this series[1] the hypothesis was presented that all known reactions between ozone (an electrophile) and amines (nucleophiles) can be explained on the basis of the initial formation of an adduct (I, eq 1) for which there are at least three major fates: (1) loss of molecular oxygen to give an amine oxide (II, eq 2) or further reaction products thereof; (2) an intramolecular side-chain oxidation (eq 3a or b) to give molecular oxygen and further reaction products of III; (3) dissociation to cation and anion radicals (eq 4), followed by stabilizing reactions thereof.

Equation 3a is based on a recent suggestion of Kolsaker and Meth-Cohn[2a] and is analogous to the accepted mechanism of the Polonovski reaction.[2b]


(1)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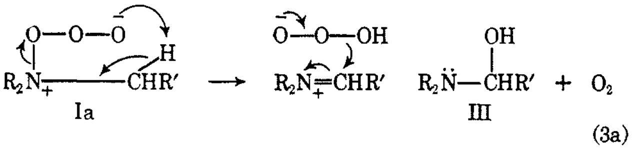
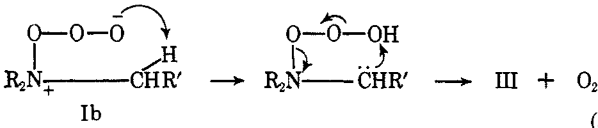
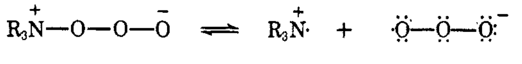

(3a)


(3b)



$$R_3\overset{+}{N}-O-O-\overset{-}{O} \rightleftharpoons R_3\overset{+}{N}\cdot + \cdot\ddot{O}-\ddot{O}-\ddot{O}:^- \quad (4)$$

Equation 3b bears an analogy to the accepted mechanism of the Steven's rearrangement.[2c]

The conversion of tertiary amines into amine oxides

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[1] P. S. Bailey, J. E. Keller, D. A. Mitchard, and H. M. White, paper presented at the International Oxidation Symposium, San Francisco, Calif., Aug 1967; Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

[2] (a) P. Kolsaker and O. Meth-Cohn, *Chem. Commun.*, **18**, 423 (1965); (b) R. Huisgen, F. Bayerlein, and W. Heydkamp, *Chem. Ber.*, **92**, 3223 (1959); (c) C. R. Hauser and S. W. Kantor, *J. Amer. Chem. Soc.*, **73**, 1437 (1951).

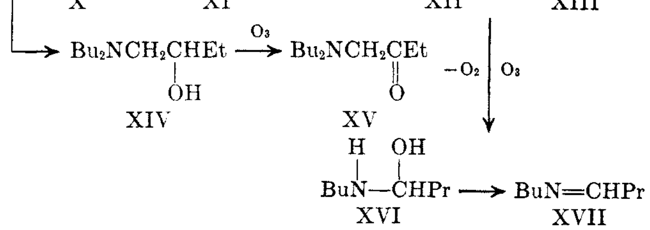
TABLE I
OZONATION OF TRI-*n*-BUTYLAMINE[a]

	Solvent						
	Pentane	CCl_4	CH_2Cl_2	$CHCl_3$	$CHCl_3$	$CHCl_3$	CH_3OH
Temp, °C	−45	−25	−45	−25	−45	−65	−45
O_3 reacting/amine reacting	1.6	1.4	1.4	1.3	1.2	1.1	1.2
O_2 evolved/O_3 reacting	0.9	...	...	...	1.0	...	...
$Bu_3\overset{+}{N}\overset{-}{O}$, %	6	11	36	38	53	65	53
$Bu_2\overset{+}{N}H_2Cl^-$, %	0	29	4	8	7	7	0
Bu_2NH_2, %	22	2	17	14	10	5	9
$BuN{=}CHPr$, %	4	1	1	2	2	1	2
$Bu_2NCH{=}CHEt$, %	27	1	15	13	12	3	11
$Bu_2NCH{=}O$, %	12	10	5	7	3	2	3
$Bu_2N\overset{O}{\overset{\|}{C}}Pr$, %	9	12	9	8	6	4	6
$Bu_2NCH_2\overset{O}{\overset{\|}{C}}Et$, %	1	1	1	1	1	...	1
PrCHO	*b*	*b*	*b*	*b*	*b*	*b*	*b*
EtCOOH	*b*	*b*	*b*	*b*	*b*	*b*	*b*
PrCOOH	*b*	*b*	*b*	*b*	*b*	*b*	*b*
Total yield, %	81	67	88	91	94	87	85

[a] The ozonations were carried out with 22 mmol of ozone in an ozone–nitrogen mixture on solutions of 22 mmol of tributylamine in 50 ml of solvent. Yields were based on the amount of amine which reacted (unrecovered). [b] Present.

(eq 1 and 2),[3–8] phosphines and arsines into similar oxides,[5,8] phosphites into phosphates,[9] sulfides into sulfoxides,[8] and sulfoxides into sulfones,[8] by means of ozone, is well known. The solvents generally employed in the conversion of tertiary amines into amine oxides have been chloroform or methanol.[4,5] Following a clue from Strecker and Baltes,[3] Henbest and Stratford[6] reported a strong solvent effect in the ozonation of tri-*n*-butylamine (IV). Whereas in methanol and chloroform, 52 and 61% yields, respectively, of the amine oxide were reported, the oxide yields were only 2 and 0.5% in butyl chloride and pentane, respectively, at the same temperature (−45°). The other products (IX, X, and XII) were from oxidation of a butyl side chain, presumably *via* intermediate VIII, as shown in Scheme I. Temperature effects also have been noted in the ozonation of tertiary amines.[6,7]

SCHEME I



The present paper deals with evidence for the fate of the amine–ozone adduct (Ia or b) described by eq 3a or b, as an explanation for side-chain oxidation, and with the competition between amine–oxide formation and side-chain oxidation (eq 2 and 3). Since Henbest and Stratford[6] carried out their ozonations with ozone–oxygen mixtures, the possibility was not eliminated that the side-chain oxidation observed resulted from autoxidation. Thus, the ozonation of tributylamine (IV) has been studied with ozone–nitrogen mixtures in pentane, methylene chloride, chloroform, carbon tetrachloride, and methanol. The chloroform experiments were carried out at three different temperatures. The results of experiments in which the best accounting of starting material was obtained are shown in Table I.

It is perhaps noteworthy that our yields of tri-*n*-butylamine oxide (VI) in chloroform at −45° were not so high as those of Henbest and Stratford[6] in the same solvent and at the same temperature, although we accounted for 94% of the starting material and they only 67%. This is probably due to the fact that Henbest and Stratford[6] did not realize that di-*n*-butylammonium chloride was a product, and it was included in their yield of amine oxide, which they extracted with water and converted into a picrate. Horner, *et al.*,[5] reported even higher oxide yields (70% for VI). The work-up procedure described does not preclude the possibility that unreacted starting material (as the picrate) was included in the amine oxide yield. In our determination of the amine oxide (VI) the more exact and specific titanium trichloride method[10] was employed. Other differences in our results and those of Henbest and Stratford[6] include our determination of products VII and XVII (Scheme I), which made possible a considerably greater accounting of starting material than obtained by the earlier workers.

Preliminary experiments in our laboratory showed that there were only minor differences in results using ozone–nitrogen and ozone–oxygen mixtures, especially in regard to the ratios of ozone to amine reacting and of

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[3] W. Strecker and M. Baltes, *Chem. Ber.*, **54**, 2693 (1921).

[4] A. Maggiolo and S. J. Niegowski, Advances in Chemistry Series, No. 21, American Chemical Society, Washington, D. C., 1959, p 202.

[5] L. Horner, H. Schaefer, and W. Ludwig, *Chem. Ber.*, **91**, 75 (1958).

[6] H. B. Henbest and M. J. W. Stratford, *J. Chem. Soc.*, 711 (1964).

[7] G. P. Shulman, *Can. J. Chem.*, **43**, 3069 (1965).

[8] P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

[9] Q. E. Thompson, *J. Amer. Chem. Soc.*, **83**, 845 (1961).

[10] (a) R. T. Brooks and P. D. Sternglanz, *Anal. Chem.*, **31**, 561 (1959); (b) G. L. K. Hoh, D. O. Barlow, A. F. Chadwick, D. B. Lake, and S. R. Sheeran, *J. Am. Oil Chemists' Soc.*, **40**, 268 (1963).

TABLE II
OZONATION OF Bu_2NCH_2COEt (XV)[a]

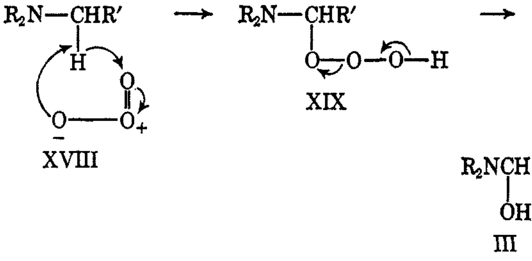
	Solvent		
	Chloroform, mmol (%)	Pentane, mmol (%)	Source
O_3	5.2	5.0	
XV reacting	4.1	4.0	
O_3/XV (reacting ratio)	1.3	1.3	
$Bu_2\overset{O^-}{N}CH_2COEt$	0.24 (6)	0.12 (3)	
Bu_2NH_2 (XII)	0.89 (22)[b,c]	0.61 (15)[c]	Eq 6, 10
Bu_2NCHO (X)	0.36 (18)[d]	0.41 (20)[d]	Eq 6, 8, 10–12
$Bu_2NCOCOEt$ (XXIV)	0.38 (9)	0.62 (16)	Eq 6, 9
$PrCON(Bu)CH_2COEt$ (XXII)	0.57 (14)	0.40 (10)	Eq 6, 7
$PrCONBu_2$ (IX)	0.02 (1)[d]	0.02 (1)[d]	Eq 6, 8, 10, 11
PrCHO (XIII)	1.25 (30)	0.74 (19)	Eq 6, 8, 10, 13
Other products	*e*	*e*	
Total yield, %	100	84	

[a] All ozonations were carried out with ozone–nitrogen mixtures on 10-mmol samples of XV in 20 ml of solvent at −45°. [b] Includes 0.15 mmol (4%) in form of dibutylammonium chloride. [c] Includes 0.02 mmol of a further oxidation product of dibutylamine (*i.e.*, BuN=CHPr; see eq 14). [d] Since these products are secondary products derived from two different primary sources, the percentage yield in accounting for the starting material is twice that based on the yield in millimoles (see eq 11 and 12). [e] Propionic acid (XXV), 17–18%, was also obtained, but is not counted in total yield since it must come from same source as certain other products (see eq 10 and 12).

amine oxide to side-chain oxidation products obtained. This result seems to exclude the possibility of a radical-type hydrogen abstraction as a step in the side-chain oxidation. If such occurred, the yield of side-chain oxidation products should be greater in the presence of oxygen than in its absence owing to the initiation of autoxidation,[11] at least in chloroform solvent where such a difference would be noticeable.

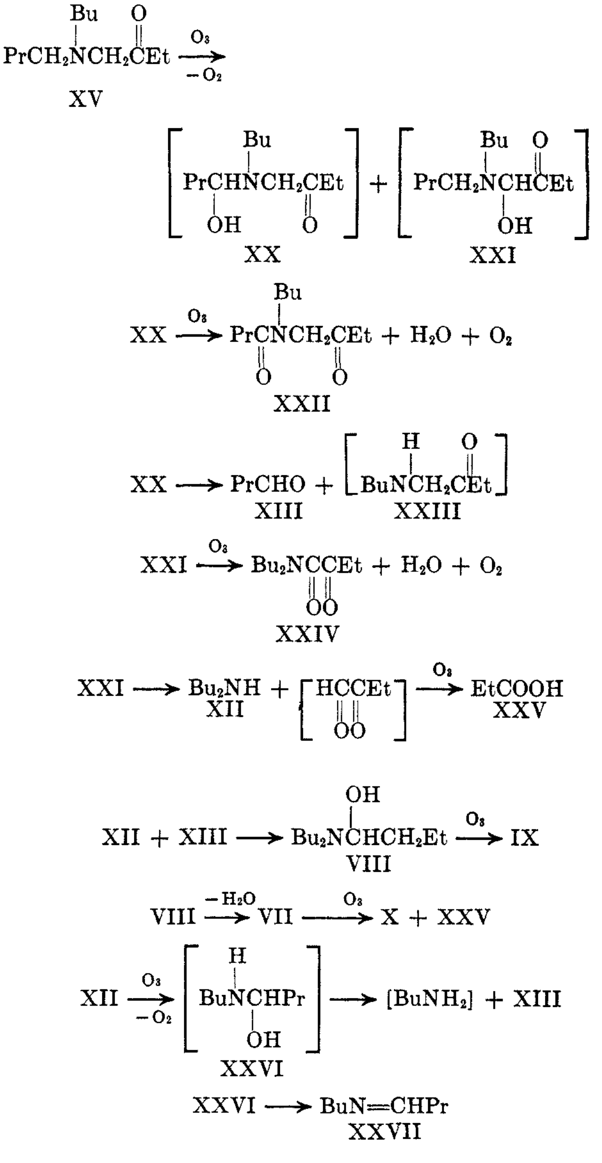
The results shown in Table I, obtained with ozone–nitrogen mixtures, not only confirm the solvent and temperature effects reported by earlier workers,[6,7] but give more information concerning them. The amine oxide yields were greatest in methanol and chloroform, next in methylene chloride, and least in carbon tetrachloride and pentane. In chloroform the amine oxide yields increased as the temperature was decreased. The ozone to amine reacting ratio varied from 1.1 to 1.6 and increased as the yield of side chain oxidation products increased. In both chloroform and pentane, the ratio of molecular oxygen evolved to ozone reacting was approximately unity.

Besides the mechanisms for side-chain oxidation of amines described by eq 3a and b, another major possibility must be considered. This is the 1,3-dipolar insertion reaction (XVIII → XIX → III) proposed recently[11] to account for results obtained upon ozonation of aromatic aldehydes,[11] aliphatic ethers,[12] anthrones,[13] and hydrocarbons.[14] To distinguish between the two possibilities, 1-di-*n*-butylamino-2-butanone (XV) was synthesized and ozonized in chloroform and in pentane. If the insertion mechanism is correct, the ozone attack should occur predominantly at the least acidic carbon–hydrogen bonds in the molecule.[11,13] These would be in the *n*-butyl groups. If, however, one of the mechanisms of eq 3a and b is operative, the most acidic nearby carbon–hydrogen bond should be attacked. This would be the methylene group between the nitrogen and carbonyl groups. The results of this study are shown in Table II.



(5)

The probable sources of the products listed in Table II are shown by eq 6–14. The minimum and maximum percentages in which these products could originate from the butyl and butanone groups of the starting material (XV) are shown in Table III. It can be seen from Table III that a minimum of 43% of the product yield arises from attack on the butanone group (*via* XXI) of 1-di-*n*-butylamino-2-butanone (XV) in both chloroform and pentane solvents and that this conceivably could be as high as 85–90%. The principal uncertainty is in regard to the source of butyraldehyde (XIII). As can be seen from eq 8, butyraldehyde (XIII) is a pri-



$$\underset{\text{XV}}{PrCH_2\overset{Bu}{N}CH_2\overset{O}{C}Et} \xrightarrow[-O_2]{O_3} \underset{\text{XX}}{\left[Pr\underset{OH}{C}H\overset{Bu}{N}CH_2\underset{O}{C}Et\right]} + \underset{\text{XXI}}{\left[PrCH_2\overset{Bu}{N}\underset{OH}{C}H\overset{O}{C}Et\right]} \tag{6}$$

$$\text{XX} \xrightarrow{O_3} \underset{\text{XXII}}{Pr\underset{O}{C}\overset{Bu}{N}CH_2\underset{O}{C}Et} + H_2O + O_2 \tag{7}$$

$$\text{XX} \longrightarrow \underset{\text{XIII}}{PrCHO} + \underset{\text{XXIII}}{\left[Bu\overset{H}{N}CH_2\overset{O}{C}Et\right]} \tag{8}$$

$$\text{XXI} \xrightarrow{O_3} \underset{\text{XXIV}}{Bu_2N\underset{O}{C}\underset{O}{C}Et} + H_2O + O_2 \tag{9}$$

$$\text{XXI} \longrightarrow \underset{\text{XII}}{Bu_2NH} + \left[H\underset{O}{C}\underset{O}{C}Et\right] \xrightarrow{O_3} \underset{\text{XXV}}{EtCOOH} \tag{10}$$

$$\text{XII} + \text{XIII} \longrightarrow \underset{\text{VIII}}{Bu_2N\overset{OH}{C}HCH_2Et} \xrightarrow{O_3} \text{IX} \tag{11}$$

$$\text{VIII} \xrightarrow{-H_2O} \text{VII} \xrightarrow{O_3} \text{X} + \text{XXV} \tag{12}$$

$$\text{XII} \xrightarrow[-O_2]{O_3} \underset{\text{XXVI}}{\left[Bu\overset{H}{N}\underset{OH}{C}HPr\right]} \longrightarrow [BuNH_2] + \text{XIII} \tag{13}$$

$$\text{XXVI} \longrightarrow \underset{\text{XXVII}}{BuN{=}CHPr} \tag{14}$$

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[11] H. M. White and P. S. Bailey, *J. Org. Chem.*, **30**, 3037 (1965).

[12] C. C. Price and A. L. Tumolo, *J. Amer. Chem. Soc.*, **86**, 4691 (1964).

[13] J. E. Batterbee and P. S. Bailey, *J. Org. Chem.*, **32**, 3899 (1967).

[14] *Cf.* ref 13 and G. A. Hamilton and B. S. Ribner, Paper given at International Oxidation Symposium, San Francisco, Calif., Aug 1967; Advances in Chemistry Series, in press.

TABLE III

ORIGINS OF PRODUCTS IN TABLE II

	Chloroform				Pentane			
	Butyl (*via* XX)		Butanone (*via* XXI)		Butyl (*via* XX)		Butanone (*via* XXI)	
	Min[a]	Max[a]	Min[a]	Max[c]	Min[a]	Max[a,b]	Min[a]	Max[a,b]
Bu_2NH (XII)	0	0	23	23	0	0	15.5	(>15.5)
Bu_2NCHO (X)	0	9.5	9.5	19	0	(>10)	10	(>20)
$Bu_2NCOCOEt$ (XXIV)	0	0	10	10	0	0	16.5	(>16.5)
XXII	15	15	0	0	10	(>10)	0	0
$PrCONBu_2$ (IX)	0	0.5	0.5	1	0	(>0.5)	0.5	(>1)
PrCHO (XIII)	0	32	0	32	0	(>20)	0	(>20)
Total	15	57	43	85	10	(57.5)	42.5	(90)

[a] The values are percentages of minimum and maximum attack on the above group in XVs, based on the percentages of each product present in the mixture of side-chain oxidation products. [b] Since in pentane only an 84% accounting of starting material was obtained, the maximum values could all be larger than the isolated yields, as indicated in the parentheses. Thus, the total maximum values listed are equal to 100% minus the respective minimum values shown for attack on the other group.

mary decomposition product of amino alcohol XX, which must be the initial product from oxidation of a butyl side chain (eq 6). The substance (XXIII) which should be simultaneously produced with butyraldehyde (XIII) could not be identified; perhaps it polymerizes or in some other way is destroyed.[15] Another possible source of butyraldehyde, however, is as a secondary product from oxidation of the butanone group of tributylamine. This involves decomposition of intermediate XXI to dibutylamine (eq 6 and 10), oxidation of dibutylamine (XII) to amino alcohol XXVI, and decomposition of XXVI to butylamine and butyraldehyde (eq 13). A similar uncertainty of origin is associated with products IX and X, since the most reasonable source of these products is *via* interaction of dibutylamine and butyraldehyde (eq 6, 8, 10, and 11) and further reactions of intermediate VIII (eq 11 and 12). We have shown qualitatively that ozonation of dibutylamine does produce butyraldehyde as a major product and that dibutylamine is more reactive toward ozone than is 1-di-*n*-butylamino-2-butanone (XV). Thus, some of the butyraldehyde (XIII), and also of products IX and X, undoubtedly does arise from intermediate XXI and the true value for attack on the butanone group must be somewhere between the minimum and maximum values of 43 and 85 or 90% shown in Table III. There is some indication that the true value is closer to the maximum than to the minimum value in spite of the fact that butyraldehyde is a primary product of decomposition of XX, but only a secondary product from further reactions of XXI. This will be discussed later.

Since there are two butyl groups and only one butanone group in XV, a statistical attack on these groups with no preference for one or the other should result in 67% attack on the butyl groups, to give XX, and only 33% attack on the butanone group, to give XXI (eq 6). Thus, even the minimum value of 43% attack on the butanone group signifies a greater rate of attack on the butanone than on the butyl groups, by a factor of 1.5 to 1. If the true value for attack on the butanone group is as high as 80%, as will be defended shortly, the rate of attack on the butanone group must be greater than that on the butyl groups by a factor of 8 to 1. Thus, these results furnish strong evidence for one of the mechanisms of side-chain oxidation described by eq 3 rather than by the insertion mechanism (eq 5).

In the light of such a mechanism the solvent and temperature effects in the ozonation of tributylamine (Table I) become understandable. The ability of a solvent to promote amine oxide formation certainly does not appear to be connected with its polarity. Butyl chloride was no better in this respect than pentane.[6] Instead, it appears to be due to its solvating power, or, as expressed by Henbest and Stratford,[6] its hydrogen-bonding capacity. Solvents such as chloroform and methanol, with which the highest yields of amine oxide were obtained, solvate the amine–ozone adduct (Ia or b, eq 3) and inhibit the abstraction of a proton required by eq 3. Thus, the major fate of the adduct (I) is loss of molecular oxygen to give the amine oxide, as shown by eq 2. With solvents like pentane, butyl chloride,[6] and carbon tetrachloride, however, there is no appreciable solvation and the major fate of the amine–ozone adduct (Ia or b) involves the side-chain oxidation (eq 3). The fact that methylene chloride gives results in between is in line with expectations based on its acidity and consequential ability to solvate Ia or b. The temperature effect observed both by the authors and by Shulman (with dimethyllaurylamine)[7] is also reasonable on the basis of the mechanisms of eq 3. The ability for the intramolecular hydrogen abstraction to occur in eq 3 should increase with increasing temperature in solvents such as chloroform, since at higher temperatures the deterring effect of solvation of the negative pole of Ia or b (eq 3) should be less. Amine oxide formation, therefore, should increase with decreasing temperature and side-chain oxidation should increase with increasing temperature in solvating solvents, like chloroform, at least up to a point, as found.

A striking difference in the results of ozonation of tributylamine (IV) and 1-di-*n*-butylamino-2-butanone (XV) is that there is no appreciable solvent effect with XV (*cf.* Tables I and II). This is understandable on the basis that the increased acidity of the methylene hydrogens of the butanone group causes hydrogen abstraction to occur so rapidly, by one of the mechanisms of eq 3, that amine oxide formation is essentially precluded in all solvents. Perhaps hydrogen bonding within the amine–ozone complex, between the negative oxygen and the hydrogens of the acidic methylene group, is more important than solvation by solvents like chloroform. Such reasoning leads to the conclusion that there must be an overwhelming preference for oxidation of the butanone group and that the maximum values of 85–90% in Table III are closer to the true value for attack on the butanone group than is the minimum value of 43%. To say the least, however, the fact is significant that with neither tri-*n*-butylamine

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(15) R. Fusco and L. Renieri, *Gazz. Chim. Ital.*, **78**, 435 (1948).

nor 1-di-*n*-butylamino-2-butanone does any appreciable attack occur at the β, γ, or δ carbons of the butyl groups. These should bear the least acidic hydrogens, and should be, therefore, the preferred positions of attack by the insertion mechanism.[11,13]

In addition to products VII, IX, X, XII, and XVII, from ozonation of tributylamine (IV), traces of XV were found, indicating a very minor attack at a β position of one of the butyl groups of IV. It seems possible that the mechanisms of eq 3 could occur at a β position, although not so easily as at an α position, since the transition state should involve a seven rather than a six-membered ring. Alternatively, this result may represent the extent to which the insertion mechanism competes with a mechanism of the type shown by eq 3.

The fact that some dibutylammonium chloride was produced from ozonations of tributylamine (IV) and 1-dibutylamino-2-butanone (XV) in chlorinated solvents (Tables I and II) is indicative that the fate of the amine–ozone adduct represented by eq 4 occurs to some extent.[16] The salts of IV and XV probably are initially produced, after which these amines are displaced from their salts by the stronger base, dibutylamine. It is interesting that this fate of the amine–ozone adduct (eq 4) does not occur to so great an extent, at least in methylene chloride and chloroform, as it does with *t*-butylamine.[16] This is not especially surprising, however, since there is no possibility for the occurrence of reactions 3a and b with *t*-butylamine. A greater mystery is the high yield of the ammonium salt from ozonation of IV in carbon tetrachloride (Table I). Although it has been reported that amines, themselves, react with carbon tetrachloride to give ammonium salts, the yields were very low even after 72 hr at room temperature.[17] We have shown that the reaction is negligible under our ozonation conditions. Thus, for some reason not yet apparent, the fate of the amine–ozone adduct described by eq 4 increases at the expense, primarily, of the fate described by eq 3, with tributylamine in carbon tetrachloride solvent. A comparison with the chloroform reaction at −25° (Table I) shows that this is not a temperature effect.

Finally, it should be mentioned that the stoichiometry observed in the ozonations of tributylamine (Table I) fit the reaction schemes of eq 1, 2, and 3 and Scheme I very well. In amine oxide formation, 1 mol equiv of ozone is required and 1 mol equiv of molecular oxygen is evolved. This is also true with certain of the side chain oxidation products (VII, XII), but not all. In the formation of X, IX, and XVII more ozone is required and, at least in the case of X, no oxygen would be evolved. Thus, the ozone–amine ratio should increase as the amount of side-chain oxidation increases, as observed. Similar observations can be made concerning Table II.

Experimental Section

The ozonation setup and procedures, using either ozone–oxygen or ozone–nitrogen, and the method for determining molecular oxygen yields are described in earlier publications.[18,19]

Nmr spectra were taken with a Varian Associates A-60 spectrometer using carbon tetrachloride as the solvent and tetramethylsilane as an internal standard.

Gas Chromatography.—Most analyses were made with an Aerograph Model 1520B with hydrogen flame detector and equipped with a disk integrator. A 0.125 in. × 10 ft column of 30% silicone gum rubber SE-30 on Chromosorb W was used at an initial temperature of 75°, which was increased at a rate of 8°/min up to 250°. N,N-Dibutylpropionamide was used as an internal standard in the tributylamine (IV) studies and tributylamine was the internal standard in the 1-butylamino-2-butanone (XV) studies. In all experiments except those employing chloroform as a solvent butyraldehyde was determined separately on the same 1520B chromatograph, using the same column and a benzene or dioxane internal standard. For the chloroform runs, an F & M 500 gas chromatograph and a 0.25 in. × 20 ft column packed with 15% Carbowax 20M on Chromosorb W was employed at 100°. The F & M machine was also used for propionic acid, employing a 0.25 in. × 10 ft 5% dimer acid silicon oil 550 on Haloport F column at 100°. Yields were obtained by comparisons with standard solutions of known compounds. Preparative vpc work was carried out on a Wilkins A-90-P3 Autoprep, using a 0.375 in. × 20 ft column of 15% Carbowax 20M on Chromosorb W at 250°.

Chemicals.—The tri-*n*-butylamine, di-*n*-butylamine, N,N-di-*n*-butylpropionamide, N,N-di-*n*-butylformamide, butyraldehyde, and propionic acid used were the best commercial grades available. All solvents were pure and anhydrous.

1-Di-*n*-butylamino-2-butanone (XV).—1-Chloro-2-butanone was prepared from propionyl chloride, diazomethane, and dry hydrogen chloride by the general method of McPhee and Klingsberg[20] [bp 66–68° (55 mm); n^{15}_{D} 1.4330; 75% yield]. This (45 g, 0.42 mol) was added to a solution of dibutylamine (163 g, 1.27 mol) in 150 ml of ethanol, and the resulting solution was refluxed for 1.5 hr. About one-half of the solvent was removed by distillation, and the residue was cooled in an ice bath. The precipitated di-*n*-butylammonium chloride was separated by filtration. The reaction mixture was diluted with ether (1–2 l.) and extracted with three 400-ml portions of dilute hydrochloric acid. The combined extracts were neutralized with potassium hydroxide pellets and extracted with three 300-ml portions of ether. The ether extract was washed with saturated salt solution, dried over anhydrous magnesium sulfate, and evaporated. The residue was distilled. After removal of a low-boiling fraction, 47 g (56% yield) of 1-dibutylamino-2-butanone (XV) was obtained: bp 92° (5 mm); n^{25}_{D} 1.4355. The infrared spectrum of a neat sample showed a strong carbonyl band at 1715 cm^{-1}; the nmr spectrum in carbon tetrachloride included peaks at τ 6.95 (singlet, two protons, $O{=}C{-}CH_2N{<}$), 7.52 (quartet, two protons, $CH_3CH_2C{=}O$), and 7.57 (triplet, four protons, $>N{-}CH_2Pr$) ppm.

Anal. Calcd for $C_{12}H_{25}NO$: C, 72.31; H, 12.64; N, 7.03. Found: C, 72.15; H, 13.05; N, 7.15.

1-Di-*n*-butylamino-1-butene (VII) was prepared as described by Henbest and Stratford:[6] bp 75° (0.7 mm); n^{25}_{D} 1.4480.

N,N-Di-*n*-butylbutyramide (IX) was prepared from di-*n*-butylamine and butyric anhydride:[21] bp 113–115° (5 mm); n^{26}_{D} 1.4445.

Butylidene butylamine (XVII) was prepared from butylamine and butyraldehyde:[22] bp 52° (21 mm); n^{25}_{D} 1.4176.

1-Di-*n*-butylamino-1,2-butanedione (XXIV) was isolated from the ozonation reaction mixture of 1-dibutylamino-2-butanone (XV) by preparative vpc. Its infrared spectrum (liquid film) showed carbonyl peaks at 1715 (keto) and 1645 cm^{-1} (amide). Its nmr spectrum (neat liquid) included peaks at τ 6.59 (triplet, four protons, $PrCH_2N{-}C{=}O$), 7.17 (quartet, two protons, $CH_3CH_2{-}C{=}O$) ppm. Peaks in the mass spectrum appeared at *m/e* 214 (mol wt + 1), 156 (mol wt − *n*-Bu or EtCO), and 128 (mol wt − EtCOCO), but not at *m/e* 142 (mol wt − PrCO).

Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.57; H, 10.87; N, 6.57. Found: C, 67.22; H, 10.68; N, 6.84.

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1-(*n*-Butyl-*n*-butyrylamino)-2-butanone (XXII) was isolated from the ozonation reaction mixture of 1-dibutylamino-2-butanone (XV) by preparative vpc. Its infrared spectrum (liquid film) showed carbonyl peaks at 1730 (ketone) and 1642 cm^{-1} (amide). Its nmr spectrum (neat liquid) included peaks at τ 5.98 (singlet, two protons, $O{=}C{-}CH_2N{<}$), 6.70 (triplet, two protons, $>NCH_2Pr$), 7.66 (complex, four protons, $EtCH_2{-}C{=}O$ and $CH_3CH_2C{=}O$), and 8.55 (complex, six protons, $O{=}CCH_2CH_2CH_3$ and $-CH_2CH_2CH_2CH_3$) ppm. Peaks appeared in the mass spectrum at *m/e* 214 (mol wt + 1), 213 (mol wt), 184 (mol wt − Et), 156 (mol wt − EtCO or Bu), and 142 (mol wt − PrCO).

Anal. Calcd for $C_{12}H_{23}NO_2$: N, 6.57. Found: N, 6.24.

Ozonation of Tri-*n*-butylamine (IV).—A solution of 4 g (21.6 mmol) of tributylamine (IV) in 50 ml of the solvent was treated with 1 mol equiv of ozone from an ozone–nitrogen mixture at −45°. The ozone absorption was quantitative. The reaction mixture was allowed to warm to room temperature and was analyzed for aldehydes by vpc. If the solvent was pentane, the reaction mixture was then extracted with three 15-ml portions of water. When the solvent was methanol, chloroform, methylene chloride, or carbon tetrachloride, the solvent was first removed under reduced pressure and 50 ml of pentane was added before the water extraction. Otherwise the separation of amine oxide from other products was incomplete. The water extract was diluted to 50 ml. The aqueous solution (5 ml) was used for the amine oxide determination by the titanium chloride method.[10] In those cases where the original solvent was a chlorinated hydrocarbon, 5 ml of the aqueous solution was used for the amine hydrochloride (ammonium salt) determination, by titration with 0.1 *N* silver nitrate solution after addition of 0.5 ml of saturated sodium bicarbonate solution and some potassium chromate indicator. The remaining water extract was made basic with sodium hydroxide and continuously extracted with ether for 24 hr. Analysis of the ether extract by vpc showed largely dibutylamine. The basic extract was acidified with hydrochloric acid and continuously extracted with ether for 24 hr. The ether extract was analyzed for carboxylic acids by vpc. The pentane layer was analyzed by vpc for the other volatile products and unreacted tributylamine.

Ozonation of 1-di-*n*-butylamino-2-butanone (XV) was carried out in the same manner as described for tributylamine.

Registry No.—IV, 102-82-9; XV, 16656-38-5; XXII, 16656-39-6; XXIV, 16656-40-9.

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Ozonation of Amines. III. *t*-Butylamine[1]

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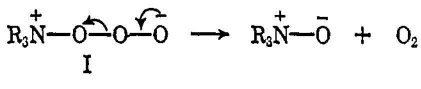
Ozonation of *t*-butylamine in chlorinated solvents gave as major products *t*-butylammonium chloride, 2-methyl-2-nitropropane, and *t*-butyl isocyanate. In isooctane, the nitroalkane and azoxyisobutane were produced, along with 2,4,4-trimethyl-2-pentanol. All amine ozonations were carried out under conditions whereby neither ozone nor the amine alone reacted appreciably with the solvent. The results are explained in terms of an initial electrophilic ozone attack on the amine to give an adduct which can either lose molecular oxygen or dissociate to nitrogen cation radicals and the ozonate anion radical.

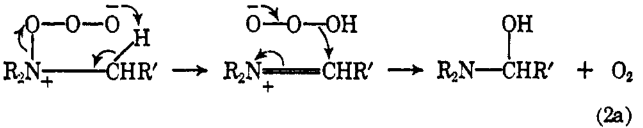
In the preceding paper[1] of this series, evidence was presented to show that the competition observed between amine oxide formation and side-chain oxidation during ozonation of certain tertiary amines involves two competing fates of an initial amine–ozone adduct (I), as illustrated in eq 1 and 2a or b. In the first paper of the series[2] a third fate of adduct I was proposed, namely, dissociation into nitrogen cation radicals and the ozonate anion radical (eq 3), followed by further reactions of these species. The formation of Wurster's salts by ozonation of phenylene diamines[3] and of ammonium ozonate by ozonation of liquid ammonia[4] are apparent examples of this reaction course open to I.

To gain further information concerning the possibility of the fate of I exemplified by eq 3, the ozonation of *t*-butylamine in several different solvents was studied. In this case there is little possibility of the occurrence of routes 2, since they would have to involve a β position. The principal competition, therefore, should be between the reactions described by eq 1 and 3.

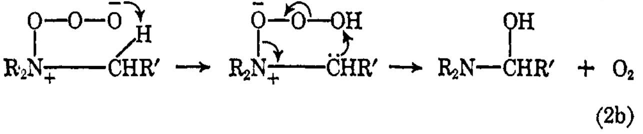
Since our first report on this work, at the International Oxidation Symposium in 1967,[2] Bachman and Strawn[5] have reported the oxidation of several different primary amines to the corresponding nitro compounds by means of ozone. The present paper describes a more thorough study of a primary amine in which all products are described and reasonable reaction paths thereto suggested. Together, these two works constitute the first detailed study of the ozonation of primary amines.[6]



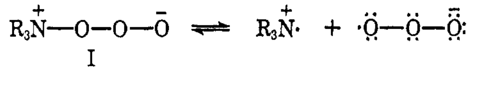
$$\underset{\text{I}}{R_3\overset{+}{N}-O-O-\overset{-}{O}} \longrightarrow R_3\overset{+}{N}-\overset{-}{O} + O_2 \qquad (1)$$



(2a)



(2b)



$$\underset{\text{I}}{R_3\overset{+}{N}-O-O-\overset{-}{O}} \rightleftharpoons R_3\overset{+}{N}\cdot + \cdot\ddot{O}-\ddot{O}-\overset{-}{\ddot{O}}: \qquad (3)$$

Experimental Section

Equipment and Procedures.—The ozonation setup and procedures, using ozone–oxygen or ozone–nitrogen, and the method of determining molecular oxygen yields are described in earlier

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[1] For paper II of this series, see P. S. Bailey, D. A. Mitchard, and A. Y. Khashab, *J. Org. Chem.*, **33**, 2675 (1968).

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