

Faust spinning-band column to yield 151 g of analytically pure product (Table I).

**Rate Measurements.**—Gas chromatographic analyses were performed using a Beckman GC-2A gas chromatograph, equipped with a 10-in. recorder and Disc integrator, and containing a 2 ft  $\times$  0.25 in. column of 30% silicone 550 on 42–60 mesh firebrick. Concentrations were obtained as a function of time by comparing the integrated area of a reactant peak at time  $t$  with the area of that peak at time  $t_0$ . Since the  $t_0$  peak corresponded to a known initial concentration, the actual concentration at time  $t$  was found from the ratio of peak areas.

In a typical run,  $2.00 \times 10^{-4}$  mol of glycidyl ether and  $2.00 \times 10^{-4}$  mol of dibutylamine were weighed into a 10-ml volumetric flask, and enough  $t$ -amyl alcohol was added to bring the total volume to exactly 10 ml.<sup>16,17</sup> The solution was then immediately transferred to a round-bottom flask equipped with a magnetic stirrer and a self-sealing rubber septum cap. The flask was capped and placed in a constant temperature bath, which was maintained at the reaction temperature  $\pm 0.05^\circ$ . The  $t_0$  reading was then taken by piercing the septum cap with a syringe and withdrawing a 10.0- $\mu$ l aliquot, which was injected directly into the gas chromatograph for analysis. Subsequent 10.0- $\mu$ l samples were withdrawn at various times and analyzed in an identical manner. Variation in the height of the sharp  $t$ -amyl alcohol peak, which served as an internal standard, was generally less than 1% during a run, and never more than 2.5%. All reactions were followed to at least 60% completion.

Each of the reactions was run at three different temperatures (41.0, 51.0, and 60.0 $^\circ$ ) using initial concentrations of 0.200 *M* in  $t$ -amyl alcohol for each reactant. All of the 60 $^\circ$  reactions were run in duplicate. Rate constants were reproducible to within 1% in most cases, and to within 3% in the least favorable case.

**Product Analysis.**—Product investigation was done by glpc analysis of the infinite-time kinetic samples. A 6 ft  $\times$  0.25 in.

(16) In an unpublished study involving neat solutions of dibutylamine and the glycidyl ethers above, we have shown that the error introduced by allowing the reactants to be in contact during weighing is about 0.1%. This slight error has been ignored in our measurements.

(17) Initial concentrations were corrected for the expansion of the solution upon heating from room temperature to reaction temperature.

column packed with 30% Ucon 50 HB 2000 on 42–60 mesh firebrick was used for analytical and preparative work.

Glpc analysis of the reaction mixtures indicated a single, sharp product peak for each of the reactions. After purification by preparative glpc, these products were characterized by their nmr spectra as the "normal" isomers (products of terminal attack by the amine on the epoxide ring). No trace of the second (abnormal) isomer could be found in any of the systems. In each case, the ratio of the nmr integral of the N–C–H vs. O–C–H protons was 2:1, corresponding to that required for the normal isomer.

Since all products are identical on the amino side of the glycidyl ether oxygen, the features of interest in their spectra are extremely similar. These features are illustrated by the following example.

**Adduct of Dibutylamine and Glycidyl Ether 1c.**—The reaction product had a retention time of 2.5 min at 35 psig,  $T = 200^\circ$ , on the column described above. Its nmr spectrum showed maxima at  $\delta$  6.73 (triplet of triplets, 1, Ar–H), 4.18 (d, 2, O–CH<sub>2</sub>) 3.83 (m, 1, CHO–H), 3.60 (s, 1, O–H), 2.52 (m, 6, N–CH<sub>2</sub>), 1.36 (m, 8, C–CH<sub>2</sub>), 0.93 (t, 6, CH<sub>3</sub>).

The infrared spectrum showed absorptions at 3440 cm<sup>-1</sup> (hydroxyl); 2900, 1460 (C–H); 1640, 1540, and 1490 (aromatic); 1175 (Ar–O–R); and 1100 (C–F, alcoholic C–O).

**Registry No.**—1a, 122-60-1; 1b, 585-45-5; 1c, 25056-10-4; 5a, 25056-11-5; 5b, 25056-12-6; 5c, 25056-13-7; 5d, 25080-58-4; 2-(3-trifluoromethylphenyl)hexafluoro-2-propanol, 25056-14-8; 2-[3,5-di(trifluoromethyl)phenyl]hexafluoro-2-propanol, 25056-15-9; 2-(pentafluorophenyl)hexafluoro-2-propanol, 13732-52-0; adduct of dibutylamine and glycidyl ether 1c, 25056-17-1.

**Acknowledgment.**—We wish to thank Mr. C. F. Poranski and Dr. W. B. Moniz for running the nmr spectra.

## Ozonation of Amines. IV.<sup>1</sup> Di-*t*-butylamine

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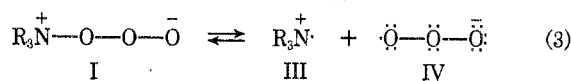
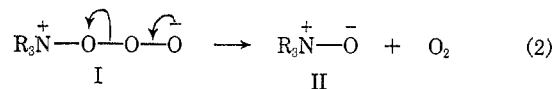
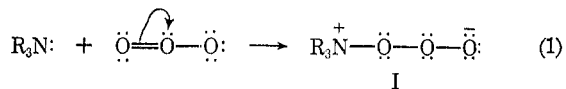
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Results of a thorough study of the ozonation of a secondary amine, di-*t*-butylamine, are reported for the first time. The major final products from ozonation in chloroform are 2-methyl-2-nitropropane, di-*t*-butylammonium chloride, and various derivatives of the *t*-butyl group lost in formation of the nitro compound. In contrast to the ozonation of *t*-butylamine, the ozonate anion radical is not produced initially, but di-*t*-butyl nitroxide is. To explain these results a new (fourth) fate of the amine–ozone adduct is proposed.

The first paper of this series<sup>2</sup> initiated a systematic study of the ozonation of primary, secondary, and tertiary aliphatic amines in which the alkyl groups are varied as to whether they are primary, secondary, or tertiary. A working hypothesis was presented in the preceding papers<sup>1–3</sup> as a rationale for the reactions found both by us and others to occur during the ozonation of amines. This involved the formation of an initial amine–ozone adduct (I, eq 1) followed by three fates thereof: (a) loss of molecular oxygen with formation of an amine oxide (II, eq 2) or further reaction products thereof; (b) an intramolecular side-chain oxidation; (c) homolytic dissociation to a nitrogen cat-

ion radical (III) and the ozonate anion radical (IV, eq 3), followed by reactions of these. Paper II<sup>3</sup> reported the results of ozonation of tri-*n*-butylamine, a tertiary amine with primary alkyl groups, for which the major competitive fates of the amine–ozone adduct (I) were amine oxide formation (eq 2) and side-chain oxidation. Paper III<sup>1</sup> discussed the ozonation of *t*-butylamine, a primary amine having a tertiary alkyl group, for which the major fates of I were those of eq 2 and 3.



(1) Part III: P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968).

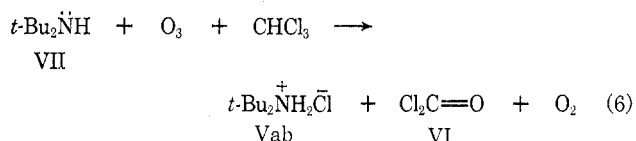
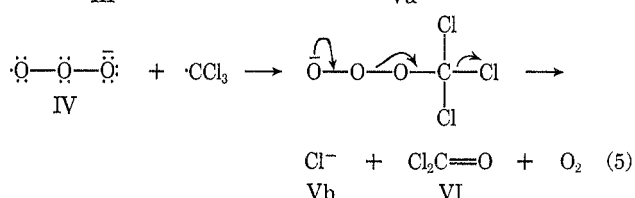
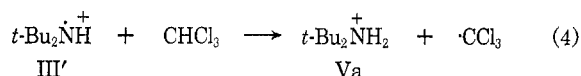
(2) P. S. Bailey, J. E. Keller, D. A. Mitchard, and H. M. White in "Oxidation of Organic Compounds. III," *Advances in Chemistry Series*, No. 77, American Chemical Society, Washington, D. C., 1968, pp 58–64.

(3) P. S. Bailey, D. A. Mitchard, and A. Y. Khashab, *J. Org. Chem.*, **33**, 2675 (1968).

The present paper deals with the first detailed study of the ozonation of a secondary amine, di-*t*-butylamine (VII), although one particular aspect of the ozonation of several aromatic and alicyclic secondary amines has previously been reported.<sup>4a</sup> In addition, the present paper presents a low-temperature epr study of the ozonation of both *t*-butylamine and di-*t*-butylamine.

The ozonations of di-*t*-butylamine were carried out in chloroform at  $-60$  to  $-65^\circ$ , methylene chloride at  $-75^\circ$ , and carbon tetrachloride at  $-20^\circ$ , usually with nitrogen as a carrier. Typical experiments are shown in Table I. As was true also in the case of *t*-butylamine,<sup>1</sup> the experiments in chloroform are easier to interpret and will be discussed first.<sup>4b</sup> The ratio of ozone (with nitrogen carrier, expt 1-3) to amine reacting was approximately equal to 2, regardless of whether excess ozone was employed or whether that used was insufficient to react with all of the starting amine. Likewise the yields of products were approximately the same in either case. This indicates that any intermediate products reacted almost as quickly as they were formed. The major products were 2-methyl-2-nitropropane (X), di-*t*-butylammonium chloride (Vab), *t*-butyl alcohol (XI), acetone, and molecular oxygen. In addition, traces of di-*t*-butyl peroxide, *t*-butyl chloride, isobutylene, and di-*t*-butyl nitroxide (VIII) were found. The sum of the yields of *t*-butyl alcohol, acetone, di-*t*-butyl peroxide, *t*-butyl chloride, and isobutylene was equal to 85-90% of the 2-methyl-2-nitropropane yield, thus accounting for most of the *t*-butyl group lost in the formation of the nitro compound. For each millimole of ozone which reacted during the ozonation, approximately 0.7 mmol of molecular oxygen was evolved.

The reactions involved in the ozonation of di-*t*-butylamine (VII) are obviously more complex than those occurring during the ozonation of *t*-butylamine.<sup>1</sup>



(4) (a) S. D. Razumovskii, A. L. Buchachenko, A. B. Shapiro, E. G. Rozantsev, and G. E. Zaikov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **133**, 1086 (1968). (b) A possible question concerns the reaction of ozone with chloroform in the absence of added substrate. In our earlier paper<sup>1</sup> we showed that ozone reacts with chloroform much more slowly than with *t*-butylamine under comparable conditions and that essentially no hydrogen chloride is produced by the reaction. Experience has shown that solvents reactive toward ozone may be used in ozonations without themselves reacting appreciably, provided the substance being ozonized is more reactive than the solvent; see P. S. Bailey, *Chem. Rev.*, **53**, 925 (1958). For example, methanol is an excellent ozonolysis solvent, even though alone it is very reactive toward ozone. In the ozonation of *t*-butylamine<sup>1</sup> chloroform was used as an effective trap for the nitrogen cation radical, just as methanol is used as a trap for the Criegee zwitterion. In the present work with di-*t*-butylamine, the ammonium chloride product is not ascribed to reaction of ozone with chloroform, since it also was obtained in similar yield from ozonation in carbon tetrachloride. The latter does not react appreciably with ozone.

Since, however, a major product from ozonation of both amines in chloroform was the corresponding ammonium chloride, one would initially assume that the mechanisms leading to the salt were the same in each case. For di-*t*-butylamine (VII), by analogy to *t*-butylamine,<sup>1</sup> this would involve eq 1-5, the summation of which produces eq 6. The odor of phosgene (VI) was strong in the reaction mixture, and it was shown independently that, whereas *t*-butylamine and phosgene react to give *t*-butyl isocyanate and/or N,N'-di-*t*-butylurea<sup>1</sup>, no urea was produced when di-*t*-butylamine and phosgene were mixed.

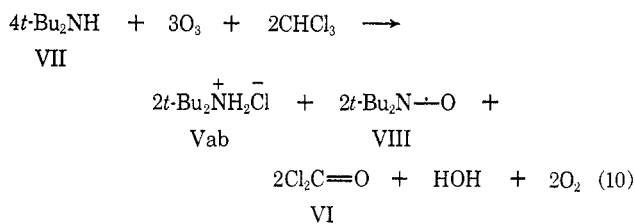
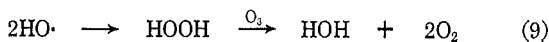
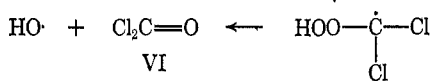
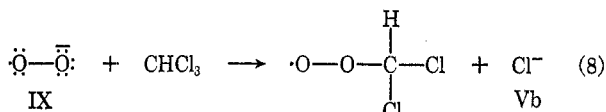
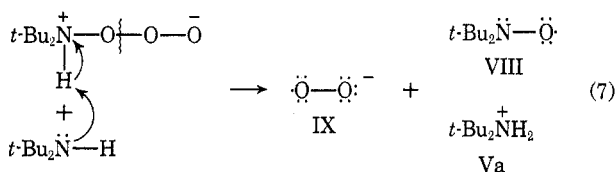
The assumption that the mechanisms leading to salt formation were the same for the ozonations of *t*-butylamine<sup>1</sup> and di-*t*-butylamine was shown to be invalid by low-temperature epr studies. Ozonation of *t*-butylamine in pentane at  $-120^\circ$  gave immediately a red solution. An epr spectrum of the solution gave a strong signal for the ozonate anion radical (IV) in the form of a singlet with a *g* value of 2.0107.<sup>5</sup> Further ozonation produced a red precipitate which, by analogy to the ozonation of ammonia,<sup>5</sup> must have been *t*-butylammonium ozonate. The singlet for the ozonate anion radical was also observed during ozonation of *t*-butylamine in methylene chloride at  $-90^\circ$ . It decayed rapidly, however. Thus, the nitrogen cation radical-ozonate anion radical (eq 3) route to *t*-butylammonium chloride during ozonation of *t*-butylamine in chlorinated solvents<sup>1</sup> was confirmed. In contrast, however, epr spectra taken during the ozonation of di-*t*-butylamine in pentane at  $-120^\circ$ , in Freon 11 (dichlorodifluoromethane) at  $-115^\circ$ , and in methylene chloride at  $-90^\circ$  showed no signal whatsoever for the ozonate anion radical (IV). Instead, the characteristic triplet for di-*t*-butyl nitroxide<sup>6,7</sup> (VIII) immediately and strongly appeared. In order to make certain that the signal for the ozonate anion radical (IV) could be observed if present, a mixture of *t*-butylamine and di-*t*-butylamine was ozonized in pentane at  $-120^\circ$ , and the reaction was monitored by epr spectroscopy. Signals for both the ozonate anion radical and di-*t*-butyl nitroxide were strongly present. This clearly shows that the amine-ozone adduct fate depicted by eq 3 does not occur to any detectable extent with di-*t*-butylamine. It also strongly suggests that di-*t*-butyl nitroxide (VIII) is a primary product of the ozonation of di-*t*-butylamine (VII). Evidence for the intermediacy of nitroxide radicals in the ozonation of secondary amines has also been reported by Razumovskii, *et al.*<sup>4a</sup> Working with certain aromatic and alicyclic amines, they reported high yields of the nitroxides in some cases.

In order to account for these facts, a fourth fate of the amine-ozone adduct (I) is proposed. This is illustrated by eq 7 followed by eq 8 and 9. If these are combined with eq 1, an overall equation is obtained (eq 10) which describes the ozonation of di-*t*-butylamine in chloroform to the corresponding ammonium salt and di-*t*-butyl nitroxide, etc.

(5) I. J. Solomon, K. Hattori, A. J. Kacmarek, G. M. Platz, and M. J. Klein, *J. Amer. Chem. Soc.*, **84**, 34 (1962), report a *g* value of 2.0119.

(6) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *ibid.*, **86**, 639 (1964).

(7) Superimposed on the nitroxide triplet was also a less intense triplet with a splitting constant equal to that reported for the 2-methyl-2-nitropropane anion radical; see A. K. Hoffman, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *ibid.*, **86**, 631 (1964).



The reactions of eq 7 provide a route both to the ammonium cation (Va) and to di-*t*-butyl nitroxide (VIII) as an initial product. The driving force would be the formation of the stable nitroxide *via* a transition state which involves both the amine-ozone adduct and a second amine molecule. The oxygen anion radical (IX) is well known and readily formed.<sup>8</sup> Its attack on the solvent is a logical route to the chloride anion (Vb) moiety of di-*t*-butylammonium chloride (Vab), as shown in eq 8. The fact that the yield of ammonium salt was very little less with carbon tetrachloride solvent (expt 6) than with chloroform and about the same as with methylene chloride (expt 5) is in agreement with this mechanism. This was not true with *t*-butylamine, where the route to salt, after the formation of the ion radicals (eq 3), was more complicated in carbon tetrachloride than in chloroform or methylene chloride.<sup>1</sup>

The oxygen anion radical (IX) could also be the cause of the formation of trace amounts of the 2-methyl-2-nitropropane anion radical,<sup>7</sup> through release of an electron to a nitroalkane (X) molecule which had been produced from ozonation of di-*t*-butyl nitroxide (VIII), as described below. Epr spectra taken during the ozonation of di-*t*-butyl nitroxide alone (in absence of di-*t*-butylamine) show no signal for the nitroalkane anion radical.

In the accompanying paper<sup>9</sup> the results of ozonation of di-*t*-butyl nitroxide (VIII) are discussed. Equation 11 portrays reasonably well the stoichiometry of the reaction. The fact that the products are essentially the same as those obtained from ozonation of di-*t*-butylamine provides added evidence for the intermediacy of di-*t*-butyl nitroxide (VIII) in the ozonation of di-*t*-butylamine (VII).

Equation 12 is a combination of eq 10 and 11. It does not portray exactly the stoichiometry of the ozonation of di-*t*-butylamine, since Table I shows that 2-

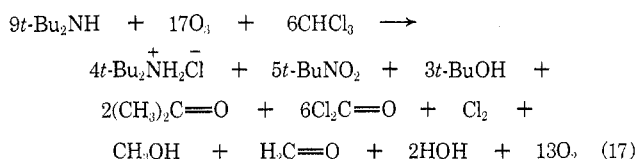
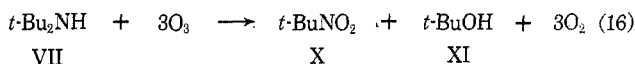
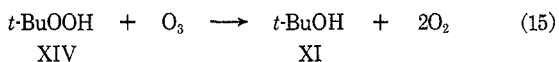
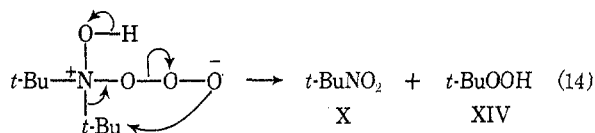
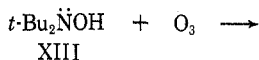
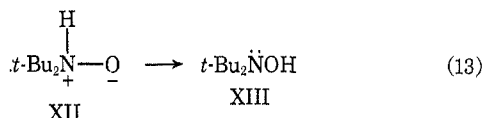
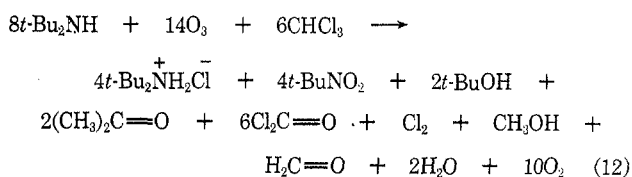
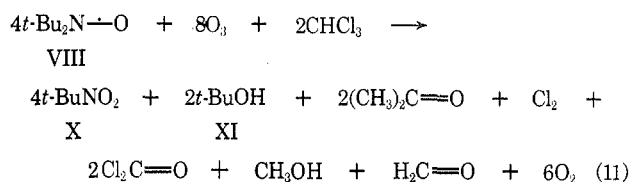
(8) D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, **37**, 1562 (1965).  
 (9) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **35**, 2782 (1970).

TABLE I  
 OZONATIONS OF DI-*t*-BUTYLAMINE

Expt	Solvent, <sup>a</sup> m	Amine, mmol		O <sub>2</sub> evolved, mmol	t-BuNO <sub>2</sub>		t-BuNH <sub>2</sub> Cl <sup>-</sup>		t-BuOH		Me <sub>2</sub> C=O		Other products,				
		Starting	Reacting <sup>b</sup>		Passed	Reacted	O <sub>3</sub> / <sup>c</sup> amine <sup>d</sup>	mmol	% <sup>e</sup>	mmol	% <sup>e</sup>	mmol	% <sup>e</sup>	mmol	% <sup>e</sup>		
1	CHCl <sub>3</sub> , 15	2.36	2.36	6.5	4.9	2.1	3.4	0.98	42	0.64	27	0.47	20	0.02 <sup>h</sup>	1	96	90
2	CHCl <sub>3</sub> , 15	2.32	2.32	6.4	5.2	2.2	i	1.01	44	0.65	28	0.40	17	0.03 <sup>h</sup>	1	98	90
3	CHCl <sub>3</sub> , 15	5.00	3.10	6.0	6.0	1.9	4.2	1.32	43	0.73	23	0.54	17	i	i	99	83
4	CHCl <sub>3</sub> , 25	2.33	2.33	5.5 <sup>f</sup>	4.3	1.8	i	0.74	32	1.00	43	0.30	13	0.03 <sup>h</sup>	1	100	89
5	CH <sub>2</sub> Cl <sub>2</sub> , 25	2.33	2.33	7.5	6.5 <sup>f</sup>	2.8 <sup>f</sup>	i	0.77	33	0.89	38	0.43	18	0.01 <sup>m</sup>	i	100	91
6	CCl <sub>4</sub> , 8	1.13	1.13	Excess	3.6	i	i	0.77	36	i	i	i	i	i	i	i	i
		1.04	1.04	5.0	3.6	i	i	i	33	i	i	i	i	i	i	i	i

<sup>a</sup> The ozonations in CHCl<sub>3</sub> solvent were carried out at -60 to -65°, the one in CH<sub>2</sub>Cl<sub>2</sub> at -75°, and those in CCl<sub>4</sub> at -20°. <sup>b</sup> The millimoles of amine reacting is equal to the millimoles of starting amine minus the millimoles of amine detected at the end of the experiment. <sup>c</sup> All ozonations except no. 4 were with ozone-nitrogen. <sup>d</sup> Ratio of ozone reacting to amine reacting. <sup>e</sup> All percentage yields are based on the amount of amine reacting. <sup>f</sup> Per cent accounting of nitrogen in products from amine reacting. <sup>g</sup> Per cent accounting in products of the second *t*-butyl group (which is lost in production of the nitro compound). <sup>h</sup> Di-*t*-butyl peroxide (0.01 mmol), *t*-butyl chloride (0.01 mmol), isobutylene (trace to 0.01 mmol). <sup>i</sup> Not determined. <sup>j</sup> Oxygen rather than nitrogen was the ozone carrier. <sup>k</sup> *t*-Butyl chloride (0.03 mmol), the rest undetermined. <sup>l</sup> Value could be slightly high. <sup>m</sup> Isobutylene (0.014 mmol), the rest undetermined.

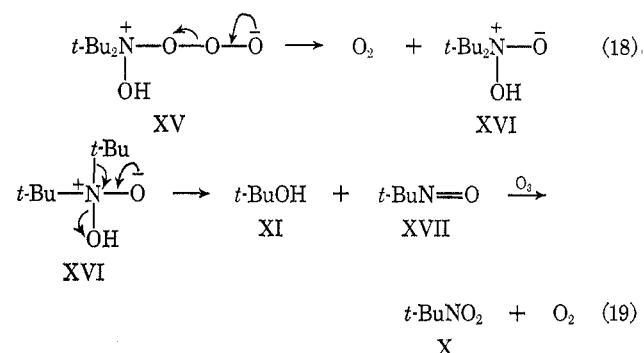
methyl-2-nitropropane (X) is always produced in larger amounts than di-*t*-butylammonium chloride (Vab). There must be some other, relatively minor, reaction occurring which yields 2-methyl-2-nitropropane during ozonation of di-*t*-butylamine (VII) without going through di-*t*-butyl nitroxide (VIII) as an intermediate. We suggest that this involves the amine oxide fate of the initial amine-ozone adduct (eq 2). Rearrangement of the amine oxide (XII) of di-*t*-butylamine to di-*t*-butylhydroxylamine (XIII, eq 13) followed by ozonation of XIII can logically give the nitro compound (X) plus *t*-butyl hydroperoxide (XIV), eq 14). Ozonation of *t*-butyl hydroperoxide is known to give *t*-butyl alcohol as the major product (eq 15), although small amounts of acetone, di-*t*-butyl peroxide, and *t*-butyl chloride are also obtained.<sup>10</sup> Combination of eq 1, 2, 13, 14, and 15 gives eq 16 as a representation of the overall reaction involving di-*t*-butylhydroxylamine as an intermediate. This combined with eq 12 gives eq 17, which in most details depicts accurately the stoichiometry of the ozonation of di-*t*-butylamine, especially the ratios of salt, nitroalkane, *t*-butyl alcohol, and acetone.



One discrepancy in eq 17, however, is that the ratio of ozone reacting to amine reacting is too low (*cf.* expt 1-2, Table I). This could result from the fact that the equation does not take into account the reactions of

ozone with methanol and formaldehyde, which certainly should occur, at least in expt 1 and 2 where the ozonation was carried essentially to completion. In expt 3 (Table I) the ozonation was not carried to completion and the ozone/amine ratio was equal to the value described by eq 17. The minor products, di-*t*-butyl peroxide, *t*-butyl chloride, and isobutylene most likely arose from ozonation of *t*-butyl hydroperoxide<sup>10</sup> (eq 15) and/or action of chlorine (eq 11) or traces of hydrogen chloride on di-*t*-butyl nitroxide.<sup>9,11</sup>

Another possible route to the nitrobutane (X) not involving di-*t*-butyl nitroxide (VIII) is represented by eq 18 and 19. This is thought to be less likely than the route represented by eq 14 and 15, however, because the blue color of the nitrosobutane (XVII) was never evident during the ozonation. In contrast, the nitrosoalkane color was strongly present during ozonation of *t*-butylamine.<sup>1</sup>

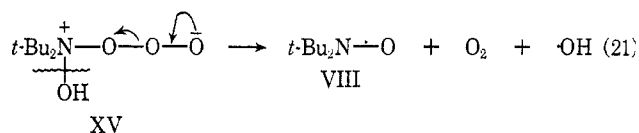
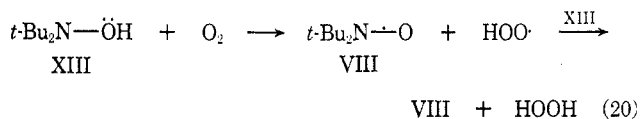


In an attempt to test the validity of reactions such as those of eq 14, 15, 18, and 19, di-*t*-butylhydroxylamine (XIII) was synthesized and ozonized. The results, which are reported in the accompanying paper,<sup>9</sup> were inconclusive owing to the great ease with which the hydroxylamine (XIII) was converted to di-*t*-butyl nitroxide (VIII) by means of oxygen, during the ordinary scale reaction, probably *via* reaction 20. Even during transfer to the ozonation vessel, the red color of di-*t*-butyl nitroxide appeared in the freshly distilled hydroxylamine. The color deepened during the ozonation, and the nitroxide was an isolable product at the end of the ozonation. Even though ozone-oxygen was employed, molecular oxygen would be present throughout the ozonation, from reactions 11, 15, and/or 18 and 19. The hydroxylamine (XIII) appears to be more reactive toward oxygen than toward ozone and, when in excess, would be expected to react with oxygen rather than ozone. Thus, we believe that considerable amounts of the hydroxylamine was converted to the nitroxide, causing the products of ozonation of the hydroxylamine, and ratios thereof, to be similar to those obtained by ozonation of the nitroxide (VIII). The situation would be quite different, however, during ozonation of di-*t*-butylamine (VIII) when the hydroxylamine (XIII) is a minor intermediate. There ozone would always be in excess both to the hydroxylamine and oxygen, and reactions such as 14 and 15 or 18 and 19 should be predominant. Another possible reaction of the hydroxylamine with ozone is shown by eq 21. Evidence that

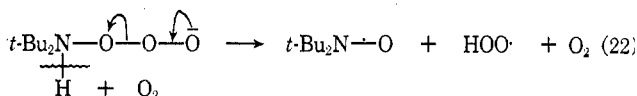
(10) D. Barnard, G. R. McSweeney, and J. F. Smith, *Tetrahedron Lett.*, No. 14, 1 (1960).

(11) (a) A. K. Hoffmann and A. T. Henderson, *J. Amer. Chem. Soc.*, **83**, 4671 (1961); (b) A. M. Feldman, private communication.

ozone does not convert the hydroxylamine (XIII) to the nitroxide (VIII), however, was obtained by following the ozonation, by epr, in methylene chloride at  $-90^\circ$  in a small-scale reaction. As ozone–nitrogen was passed into the reaction mixture, the nitroxide signal decreased in intensity or disappeared. Furthermore, eq 21 does not satisfy the stoichiometry of the di-*t*-butylamine ozonation which requires a route to the nitrobutane not involving the nitroxide (VIII).



When di-*t*-butylamine was ozonized in chloroform with ozone–oxygen (expt 4, Table I) rather than with ozone–nitrogen, a slightly lower ratio of ozone to amine reacting, higher yields of 2-methyl-2-nitropropane (X) and *t*-butyl alcohol (XI) and a lower yield of di-*t*-butylammonium chloride (Vab) were obtained. To say the least, this is further evidence against the nitrogen cation radical route to the ammonium salt (eq 3–5); the presence of oxygen does not affect the salt yield appreciably during ozonation of *t*-butylamine in chlorinated solvents. A possible explanation is a competition between the reactions of eq 7 and 22, in which oxygen is com-



peting with unreacted amine for the hydrogen of the amine–ozone adduct. The slightly lower ozone to amine ratio could be due to reaction of the minor di-*t*-butylhydroxylamine (XIII) intermediate with molecular oxygen rather than ozone, as already discussed (eq 20).

A final observation is that higher yields of 2-methyl-2-nitropropane (X) and *t*-butyl alcohol (XI) and a lower yield of di-*t*-butylammonium chloride (Vab) were obtained from ozonation of di-*t*-butylamine in methylene chloride, expt 5, compared with ozonation in chloroform. It is possible that this reflects a lower susceptibility of methylene chloride than chloroform to nucleophilic attack by the oxygen anion radical (eq 8).

### Experimental Section

**Materials.**—Di-*t*-butyl nitroxide (VIII) was prepared by the procedure of Hoffmann *et al.*,<sup>6</sup> bp  $58^\circ$  (11 mm). Di-*t*-butylamine (VII) was made by reduction of di-*t*-butyl nitroxide by the general iron–hydrochloric acid method of Johnson and Degering<sup>12</sup> for reduction of nitro compounds: 46% yield, bp  $119^\circ$ ,<sup>13</sup>  $n_D^{25}$  1.4100; nmr peak at  $\tau$  8.85. di-*t*-Butylhydroxylammonium chloride (mp  $175^\circ$ ) and di-*t*-butylhydroxylamine (XIII) were made by sodium reduction of di-*t*-butyl nitroxide, as described previously.<sup>6</sup> 2-Methyl-2-nitropropane<sup>14</sup> (X) and 2-methyl-2-

nitropropane<sup>15</sup> (XVII) were prepared by known literature procedures.

**General Equipment and Procedures.**—The ozonation setup and procedures, using ozone–oxygen or ozone–nitrogen and the method for determining molecular oxygen yields are described in earlier papers.<sup>16</sup> A Beckman IR-5A double-beam spectrophotometer was employed for infrared measurements.

**Epr Procedures.**—All spectra were recorded with a Varian Associates V-4502 spectrometer equipped with a Varian field dial and a 9-in. magnet using a modulation frequency of 100 kcps. The spectra were taken while bubbling an ozone–nitrogen stream (see above) into a special reactor made by sealing off a 25-cm length of 5-mm Pyrex tubing, blowing a bubble midway to prevent the sample from being blown out, and equipping it with a gas inlet tube made by pulling 7-mm glass tubing to capillary size and of such length that the tip came within 1 cm of the bottom of the reaction tube. For reactions in solvents with a high dielectric constant (methylene chloride), the lower part of the reaction tube was only 3 mm in diameter. The reaction mixture consisted of a 1:10 by volume mixture of the amine in pentane, Freon 11 ( $\text{CCl}_2\text{F}_2$ ), or methylene chloride; enough to fill 5 cm of the reaction tube was employed. Ozonations were carried out at  $-120^\circ$  (pentane, Freon 11) and  $-90^\circ$  (methylene chloride), and the epr spectra recorded.

**Glpc determinations** were made with a Varian Aerograph 1520B chromatograph equipped with flame ionization detectors and a Beckman recorder and integrator. A 10-ft,  $1/8$ -in. column of 20% Carbowax 20 M on acid-washed Chromosorb G was used. For determinations of isobutene, acetone, *t*-butyl alcohol, *t*-butyl chloride, 2-methyl-2-nitropropane, and di-*t*-butyl peroxide, a temperature of  $75^\circ$  and a flow rate of 20 ml/min was used; benzene was the internal standard for runs in chloroform, whereas toluene was used for the methylene chloride run. Di-*t*-butyl nitroxide and di-*t*-butylhydroxylamine were determined at  $95$  or  $110^\circ$  and 2-methyl-2-nitropropane at  $125^\circ$  with *p*-xylene as the internal standard, all other conditions remaining the same.

**Ozonation of *t*-Butylamine.** (A) **Epr Studies.**—Solutions of *t*-butylamine in methylene chloride and in pentane were ozonized at  $-90$  and  $-120^\circ$ , respectively, and epr spectra were taken during the ozonations as described above. The characteristic singlet for the ozonate anion radical, with a *g* value of 2.1017,<sup>5</sup> immediately appeared. No other radical was observable. When ozonation was discontinued with the methylene chloride reaction mixture, the singlet rapidly disappeared. When the ozonation in methylene chloride was carried out at  $-78^\circ$ , a five-line epr spectrum was observed. The outer lines were 15.5 G from the center line (which was larger than the others), and the two inner lines were 10.5 G from the center line. After the sample had remained at room temperature for 1 day, only a triplet with lines of equal intensity and splittings of 15.5 G was observed. The five-line spectrum therefore consisted of two triplets. The triplet with a splitting constant of 15.5 G was identified as that of di-*t*-butyl nitroxide by comparison of its spectrum with that of an authentic sample.<sup>6,11a,17</sup> The other triplet, which had a half-life of about 70 min at room temperature, was not identified. Similar results were obtained from ozonation of *t*-butylamine in carbon tetrachloride at  $-20^\circ$ . From ozonation of *t*-butylamine in isobutane at  $-78^\circ$ , however, two overlapping triplets were observed, one for di-*t*-butyl nitroxide with the splitting of 15.5 G and the other, thought to be for the 2-methyl-2-nitropropane anion radical, with a splitting of 26.4 G.<sup>17</sup> When the reaction mixture was allowed to come to room temperature, the signal for the nitropropane anion radical disappeared, and four new lines emerged with two on each side of the center peak, 8 and 24 G from it. These were not identified.

(B) **Ozonation of *t*-butylamine in methylene chloride at  $-95^\circ$**  gave a reddish solution which faded rapidly. Upon ozonation in pentane at  $-120^\circ$ , however, the red color deepened as the ozonation progressed, and a red precipitate formed. When the temperature was allowed to rise to  $-90^\circ$ , the red precipitate and color rapidly disappeared.

**Ozonation of Di-*t*-butylamine (VII).** (A) **Epr Studies.**—Epr spectra of solutions of di-*t*-butylamine in methylene chloride at  $-90^\circ$ , Freon 11 at  $-115^\circ$ , and pentane at  $-120^\circ$  all showed

(15) W. D. Emmons, *ibid.*, **79**, 6522 (1957).

(16) A. M. Reader, P. S. Bailey, and H. M. White, *J. Org. Chem.*, **30**, 784 (1965), and references therein.

(17) A. K. Hoffman, W. G. Hodgson, and W. H. Jura, *J. Amer. Chem. Soc.*, **83**, 4675 (1961); see also references in footnote 7.

(12) K. Johnson and E. F. Degering, *J. Amer. Chem. Soc.*, **61**, 3194 (1939).

(13) F. Klages and H. Sitz, *Ber.*, **92**, 2606 (1959).

(14) N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Amer. Chem. Soc.*, **78**, 4003 (1956).

weak signals for the di-*t*-butyl nitroxide radical (VIII). As soon as ozone was passed into the solutions, by the technique already described, the signals greatly increased. Shortly thereafter signals for the 2-methyl-2-nitrobutane anion radical<sup>17</sup> also appeared (see description under *t*-butylamine ozonation above) very weakly in the methylene chloride reaction mixture but of moderate intensity in the other two solutions. No signal for the ozonate anion radical was observed in any of these reaction mixtures. However, when a 1:4 mixture of *t*-butylamine and di-*t*-butylamine in pentane was ozonized at  $-120^\circ$  by the above technique, a strong signal for the ozonate anion radical<sup>5</sup> (see description under ozonation of *t*-butylamine, above) immediately appeared along with a weaker signal for the di-*t*-butyl nitroxide radical. *t*-Butylamine appears to be more reactive toward ozone than di-*t*-butylamine. Ozonation of di-*t*-butyl nitroxide in pentane at  $-120^\circ$  resulted in a decrease in the nitroxide triplet, but no formation of the 2-methyl-2-nitropropane anion radical signal. Epr spectra of solutions of di-*t*-butylhydroxylamine in methylene chloride, pentane, and Freon 11 at  $-90^\circ$  all showed signals for the di-*t*-butyl nitroxide radical (VIII). When ozone-nitrogen was introduced into the solution, the signal weakened in intensity or disappeared (in case of  $\text{CH}_2\text{Cl}_2$ ).

(B) **Product Determination.**—In a typical experiment, a solution of 2.36 mmol of di-*t*-butylamine (VII) in 15 ml of chloroform was ozonized at  $-60^\circ$  with an ozone-nitrogen stream containing 6.5 mmol of ozone. The amount of ozone reacting was determined by titrating the iodide trap and subtracting the amount found there from the total amount of ozone employed. A cold trap following the reaction vessel in the reaction train contained no products after the ozonation. The reaction mixture gave a positive iodide test for peroxide but a negative lead tetraacetate test for hydroperoxide.<sup>18</sup> Determinations of the liquid

(18) R. Criegee, H. Pilz, and H. Flygare, *Ber.*, **72**, 1799 (1939).

products were by glpc (see above). Di-*t*-butylammonium chloride was determined by evaporation of an aliquot of the reaction mixture to dryness and weighing the vacuum-dried residue. It was identified by comparison of its ir spectrum (Nujol mull) with that of an authentic sample; the ir spectrum also showed the absence of di-*t*-butyl hydroxylammonium chloride. The results are shown in Table I (expt 1). In another experiment the ozonation was not carried to completion. The di-*t*-butylammonium chloride was extracted from the reaction mixture with water and determined by titration for chloride with standard silver nitrate solution. Ethereal hydrogen chloride was then added to the organic layer; evaporation and determination of the residue by weighing gave the yield of unreacted di-*t*-butylamine.

**Reactions of *t*-Butylamine and Di-*t*-butylamine with Phosgene in Chloroform at  $-65^\circ$ .**—Phosgene was passed into a solution of 0.5 ml of *t*-butylamine in 8 ml of chloroform at  $-65^\circ$  for several minutes. An ir spectrum of the reaction mixture showed a strong isocyanate peak ( $2270\text{ cm}^{-1}$ ) but no urea peak. Addition of *t*-butylamine to the reaction mixture at room temperature eliminated the isocyanate peak and gave rise to a strong urea carbonyl peak ( $1630\text{ cm}^{-1}$ ). Passage of phosgene into a chloroform solution of di-*t*-butylamine under the same conditions gave no appreciable reaction, as indicated by ir spectra.

**Registry No.**—VII, 21981-37-3.

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## Ozonation of Amines. V.<sup>1</sup> Di-*t*-butyl Nitroxide

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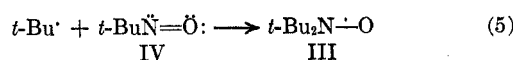
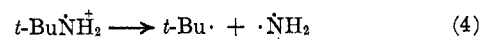
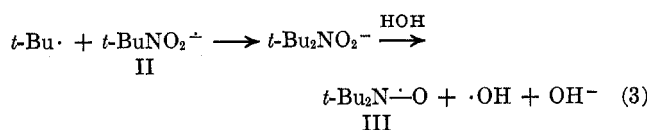
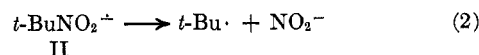
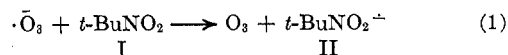
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Ozonation of di-*t*-butyl nitroxide occurs with ease giving 2-methyl-2-nitropropane and tri-*t*-butyl nitroxide as the major initial products. Ozonation of tri-*t*-butyl nitroxide gives 2-methyl-2-nitropropane, *t*-butyl alcohol, and acetone as major products. Minor products of the ozonations are 2-methyl-2-nitrosopropane, isobutene, di-*t*-butyl peroxide, and (in chloroform solution) *t*-butyl chloride and di-*t*-butylhydroxylammonium chloride. Reaction mechanisms are proposed, involving initial electrophilic ozone attacks on the nitroxides.

In earlier papers we have reported the detection of the stable radical di-*t*-butyl nitroxide<sup>2</sup> among the products of ozonation of *t*-butylamine<sup>1,3</sup> and di-*t*-butylamine.<sup>1</sup> The present paper deals largely with a study of the ozonation of this interesting stable radical, but also discusses briefly the source of the material in the above mentioned ozonations.

Di-*t*-butyl nitroxide appears to be only a minor by-product in the ozonation of *t*-butylamine;<sup>1,3</sup> although it was detected by epr in ozonations carried out at  $-78^\circ$  or higher, the only radical signal observed during ozonations carried out at  $-90^\circ$  or below was that for the ozonate anion radical.<sup>1</sup> Other products obtained in trace amounts from ozonation of *t*-butylamine in chloroform were *t*-butyl alcohol, acetone, and isobutane.<sup>3</sup> Two sources of di-*t*-butyl nitroxide during the reaction between sodium metal and 2-methyl-2-nitropropane (I) have been suggested.<sup>2</sup> One involves hydrolysis of a salt, thought to be sodium di-*t*-butyl-

hydroxylamine oxide and formed by attack of *t*-butyl radicals upon the initially formed 2-methyl-2-nitropropane anion radical (eq 3); the *t*-butyl radicals arose from decomposition of the nitroalkane anion radical (eq 2). The other source involved attack of *t*-butyl radicals on 2-methyl-2-nitrosopropane (eq 5). Either or both of these routes could also be the source of di-*t*-butyl nitroxide during ozonation of *t*-butylamine. A major product is 2-methyl-2-nitropropane<sup>3</sup> (I), and it



(1) For paper IV of this series, see P. S. Bailey, J. E. Keller, and T. P. Carter, Jr., *J. Org. Chem.*, **35**, 2777 (1970).

(2) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Amer. Chem. Soc.*, **86**, 639 (1964).

(3) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968).