[Contribution from the Shell Development Company]

Reaction of Some Aliphatic Amines with *tert*-Butyl Hydroperoxide. The Fate of the Amine

HAROLD E. De La MARE

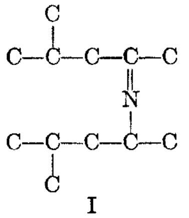
Received March 4, 1960

The oxidation of four representative amines (4-methyl-2-pentylamine, 2,4,4-trimethyl-2-pentylamine, diisopropylamine, and tri-*n*-propylamine) with *tert*-butyl hydroperoxide has been studied at 60 to 110°. It has been shown that primary and secondary amines possessing at least one *alpha* hydrogen give substituted ketimines (or aldimines) as the principal nitrogenous products when the oxidation is carried out in excess amine. Evidence is also presented to show that imines are produced when di-*tert*-butyl peroxide is decomposed in primary and secondary amine solvents. A tertiary amine, tri-*n*-propylamine, undergoes dealkylation on reaction with *tert*-butyl hydroperoxide to give di-*n*-propylamine as the major nitrogenous product. Evidence is presented which indicates the participation of free radicals.

The reduction of hydroperoxide to the corresponding alcohols in excellent yields by a number of aliphatic amines was first reported by Capp and Hawkins.[1] These authors clearly demonstrated the utility of the method for the reduction of several tertiary hydroperoxides[2]; however, neither the fate of the amine nor the mechanism of the reaction was determined. Further, it was quite apparent that information of this type was necessary to the understanding of autoxidation of simple aliphatic amines in the liquid phase,[3] a process in which hydroperoxidic intermediates are produced in the presence of a good reductant. This investigation reports a study of the interaction of four representative amines with *tert*-butyl hydroperoxide.

RESULTS

4-Methyl-2-pentylamine. The reduction of *tert*-butyl hydroperoxide by 4-methyl-2-pentylamine gave, as expected[1] excellent conversions to *tert*-butyl alcohol and water and produced a substituted ketimine (I), *N*-(4-methyl-2-pentylidene)-4-methyl-2-pentylamine, as the major nitrogeneous product (see *Table I*). However, the yield of I was observed to drop significantly as the ratio of amine to peroxide was decreased (*e.g.*, 24–41% yield at amine:peroxide ratios of ~2:1), suggesting that I is subject to further peroxide attack or, alternatively, another competitive reaction becomes increasingly important.



I

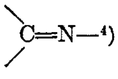
TABLE I

Products from the Reduction of *tert*-Butyl Hydroperoxide with 4-Methyl-2-Pentylamine[a]

Products	Moles	Yield, %[b]
tert-Butyl alcohol[c]	0.23	105
Water[c]	0.18	82
Ammonia	0.142	65
Gas, noncondensable[d] at −80°	≦0.015	≦7
N-(4-Methyl-2-pentylidene)-4-methyl-2-pentylamine	0.146	66
Recovered amine	0.36	—
N,N′-Bis(4-methyl-2-pentyl)oxalamide	~0.001	≦1
Unidentified (high boiling)	3.8 g.	([e])

[a] Kettle temperature, 113 to 102°; bath temperature, 110 ± 1°; amounts, 0.22 mole ROOH (82%w.), 0.74 mole RNH$_2$; reaction time, 26.5 hr.; peroxide decomposed, 98%. [b] Moles product/moles ROOH decomposed (100). [c] These values are corrected for the water and *tert*-butyl alcohol contents of the starting hydroperoxide and reflect some uncertainty in taking differences between functional group analyses. [d] Not analyzed. [e] This material probably contains *N*-(4-methyl-2-pentyl)acetamide among other amides (see Experimental).

The progress of the reaction was followed by infrared analysis with particular focus on the 5.5 to 6.5 μ region. This work demonstrated the appearance of two characteristic product bands at 5.83 μ (a carbonyl species) and 6.02 μ (a ketimine species,



[4]) As the reaction proceeded to completion, decreasing absorbance was observed at 5.83 μ and increasing absorbance at 6.02 μ. The infrared evidence suggested that I was produced from the equilibrium reaction: Further confirmation for

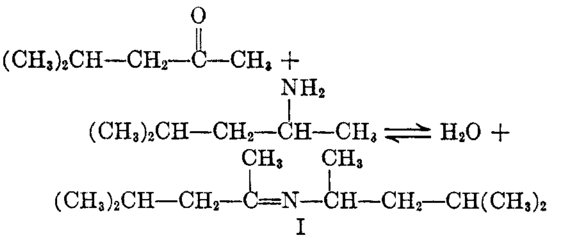
---

(1) C. W. Capp and E. G. E. Hawkins, *J. Chem. Soc.*, 4106 (1955).

(2) Although not investigated with primary and secondary hydroperoxides, it appears probable that the process will be complicated by concomitant base-catalyzed decomposition; see N. Kornblum and H. E. De La Mare, *J. Am. Chem. Soc.*, **73**, 880 (1951).

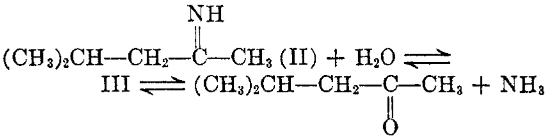
(3) Unpublished work of this laboratory.

(4) L. J. Bellamy, *Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y., 1954, p. 223.

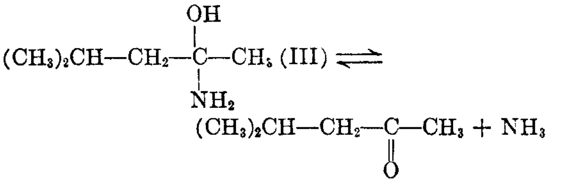


$$\mathrm{(CH_3)_2CH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + \mathrm{(CH_3)_2CH{-}CH_2{-}\overset{\overset{NH_2}{|}}{CH}{-}CH_3} \rightleftharpoons \mathrm{H_2O} + \underset{\text{I}}{\mathrm{(CH_3)_2CH{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}N{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_2{-}CH(CH_3)_2}} \quad (1)$$

(1) was obtained by demonstrating that I could be isolated (~72% yield) from 4-methyl-2-pentanone and 4-methyl-2-pentylamine under conditions simulating those in Table I. The production of ammonia in good yield suggested in turn that 4-methyl-2-pentanone came from intermediates II and/or III, (2),(3). It is impossible to choose between II



$$\mathrm{(CH_3)_2CH{-}CH_2{-}\overset{\overset{NH}{\|}}{C}{-}CH_3}\ (\text{II}) + \mathrm{H_2O} \rightleftharpoons \text{III} \rightleftharpoons \mathrm{(CH_3)_2CH{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3} + \mathrm{NH_3} \quad (2)$$



$$\mathrm{(CH_3)_2CH{-}CH_2{-}\underset{\underset{NH_2}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_3}\ (\text{III}) \rightleftharpoons \mathrm{(CH_3)_2CH{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3} + \mathrm{NH_3} \quad (3)$$

and III as primary intermediates on the basis of infrared analysis of the complex mixture, and indeed, both may participate.

The overall rate of reduction of *tert*-butyl hydroperoxide by 4-methyl-2-pentylamine was followed by periodic analysis for hydroperoxide (Figs. 1 and 2). As seen in Fig. 1, 2%w. 2,6-di-*t*-butyl-4-methylphenol is markedly effective in inhibiting the reaction. The *apparent* inhibitory effect of oxygen is shown at a lower temperature in Fig. 2. The uninhibited reaction (Fig. 1) showed an initial kettle temperature rise to 114–115° (t = 9 minutes) with a subsequent drop as the volatile reaction products accumulated. In contrast, the reaction inhibited by 2,6-di-*t*-butyl-4-methylphenol showed no initial exothermicity. An isooctane estract of the acidified phenolic-inhibited reaction mixture resulted in the isolation and identification of 2,6-di-*tert*-butyl-4-*tert*-butylperoxy-4-methylcyclohexa-2,5-dienone (IV).[5] The isolation of IV indicates the presence of *tert*-butylperoxy radicals[6] but does not preclude the participation of other radicals as well (see Discussion).

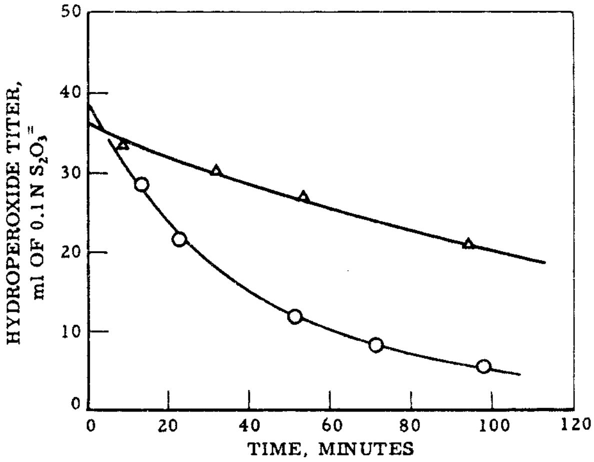


Fig. 1. Reduction of *tert*-butyl hydroperoxide by 4-methyl-2-pentylamine. Effect of 2,6-di-*t*-butyl-4-methylphenol. Bath temperature 110 ± 0.5°C, $[RO_2H]_0 \approx 1.7M$. No additive (○), kettle temperature 115 to 100°C; 2.4% 2,6-di-*t*-butyl-4-methylphenol (△), kettle temperature 110 to 108°C.

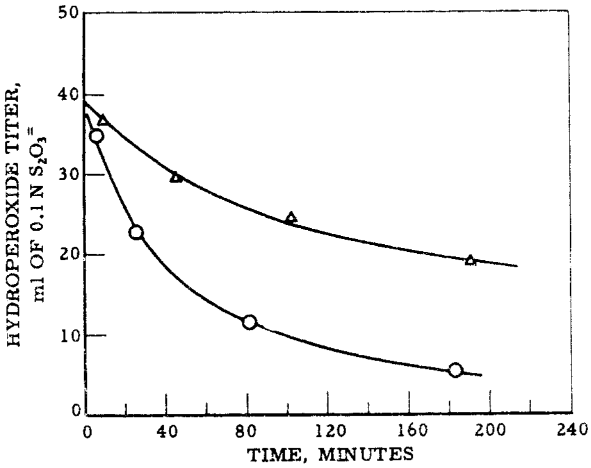
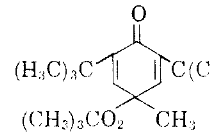


Fig. 2. Reduction of *tert*-butyl hydroperoxide by 4-methyl-2-pentylamine. Effect of oxygen, $[RO_2H]_0 \approx 1.9M$. No additive (○), bath at 95.5 ± 0.2°C, kettle at 99 to 94°C; oxygen flow (△), bath at 95.8 ± 0.2°C, kettle at 95 to 93°C



IV

2,4,4-Trimethyl-2-pentylamine (*tert-octylamine*). As a result of the observations made on the oxidation of 4-methyl-2-pentylamine, it was essential to determine the behavior of a primary amine having no *alpha* hydrogens. Therefore, the oxidation of *tert*-octylamine by *tert*-butyl hydroperoxide was examined briefly. In contrast to 4-methyl-2-pentylamine, the reaction was slow (compare Fig. 3 with Fig. 2) and the principal isolable product, 2,4,4,-trimethyl-2-nitropentane, was that of direct oxidative attack on nitrogen. The products of the oxidation of 2,4,4-trimethyl-2-pentylamine

---

(5) T. W. Campbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **74**, 1469 (1952).

(6) See the following leading references for a discussion of the inhibitory mechanism for $RO_2\cdot$ radicals. C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 and 3238 (1955); A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2220 (1956).

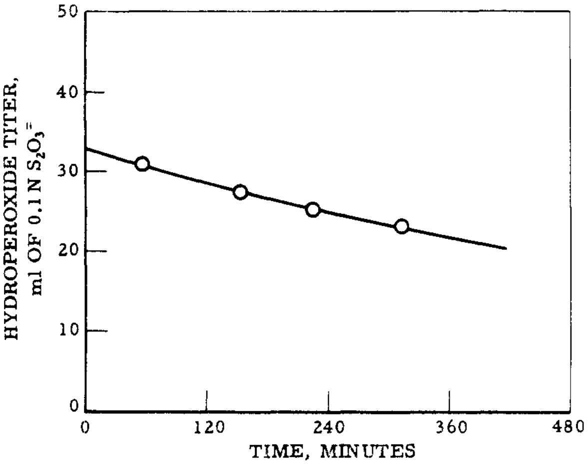


Fig. 3. Reduction of *tert*-butyl hydroperoxide by *tert*-octylamine at 95.5 ± 0.2°C, $[RO_2H]_0 \approx 1.7M$

by *tert*-butyl hydroperoxide at a somewhat higher temperature are shown in *Table II.*

TABLE II

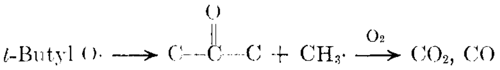
REACTION OF *tert*-OCTYL AMINE WITH *tert*-BUTYL HYDROPEROXIDE[a]

Products	Moles
tert-Butyl alcohol	0.19–0.24[b] (59–75%)
Acetone	0.02[c] (6%)
Higher boiling than *tert*-octyl amine:	
tert-Nitro octane	0.02[d]
Unidentified	4 g.[e]
Gas (noncondensable)	0.05[f]

[a] Kettle temperature, 127° to 110°C.; bath temperature, 128° ± 3°C.; amounts, 0.32 moles ROOH (88%w), 0.91 moles RNH_2; reaction time, 16 hr., peroxide decomposed, 93%. [b] Uncertainty in functional group analyses (see Experimental). [c] Acetone undoubtedly contributes to the unidentified "bottoms" through various condensation reactions either with amine or with itself. [d] Estimated by infrared analysis. [e] *Ca.* 66%w was not distillable at 140°/2 mm. (See Experimental). [f] Gases were collected in another run simulating the conditions used here; mass spectrographic analysis indicated that the principal gas produced was oxygen (91%) along with small amounts of methane (2%) and carbon monoxide (7%). Evidence was obtained for carbon dioxide production *in situ* (amine carbonate formation) but an accurate measurement of this was not obtained.

The small amount of *tert*-octylamine converted and the production of acetone, oxygen, methane, carbon dioxide, etc., suggest that a significant amount of hydroperoxide is reacting by a simple thermal path, reactions (4), (5), (6), and (7) playing a definite part.[7] Although little can be said about the mechanism of oxidation of the tertiary amine to the nitro compound, it can be concluded that primary amines having no *alpha* hydrogens react sluggishly with *tert*-butyl hydroperoxide to give poor conversions to the tertiary nitro compound.[8] As has been shown, this latter reaction is of little or no importance in the case of a primary amine possessing an *alpha* hydrogen atom.

$$t\text{-Butyl } O_2H \longrightarrow t\text{-Butyl } O\cdot + OH\cdot \tag{4}$$



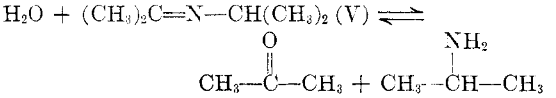
$$t\text{-Butyl } O\cdot \longrightarrow C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C + CH_3\cdot \xrightarrow{O_2} CO_2,\ CO \tag{5}$$

$$R\cdot + t\text{-Butyl } O{-}OH \longrightarrow t\text{-Butyl } O_2\cdot + RH \tag{6}$$

$$2\ t\text{-Butyl } O_2\cdot \longrightarrow t\text{-Butyl } O\cdot + O_2 \tag{7}$$

etc.

Diisopropylamine. The reduction of *tert*-butyl hydroperoxide by diisopropylamine was followed by periodic infrared analysis. Distinct absorption peaks appeared at 5.82 μ (>C=O) and 6.00 μ (>C=N—) very early in the reaction (~11% peroxide loss). These peaks were both shown to increase in intensity with decreasing hydroperoxide concentration. As the reaction proceeded (≥50% completion) the infrared spectrum showed the appearance of a peak (~0.01 mm. cell) at 6.24 μ. This latter position is compatible with that expected for a primary $—NH_2$ deformation, and is consistent with the production of isopropylamine. The infrared analysis clearly suggested ketimine formation complicated by the hydrolytic equilibrium: ketimine + $H_2O \rightleftharpoons$ amine + ketone. Initial attempts to distill the crude reaction mixture confirmed the latter postulate; a rather gradual climb in boiling point from 49°–70° was observed with attendant poor fractionation. Further, these fractions (~ b.p. ≦ 79°) showed pronounced changes in refractive index on standing at room temperature, indicating establishment of an equilibrium state. The ketone and primary amine present in these same fractions were shown to be acetone and isopropylamine by conversion to their 2,4-dinitrophenylhydrazone and *N*-phenylthiourea derivatives, respectively. *N*-(Isopropylidene)isopropylamine (V) could also be isolated in low yield by drying the low boiling fractions or the crude reaction mixture over sodium hydroxide. Thus, the equilibrium reaction is established as (8): In contrast to the similar reaction (1) found with 4-methyl-2-pentylamine, this equilibrium (8) is shifted effectively to the right during distillation because of the greater volatility of acetone and 2-propylamine. In the case of 4-methyl-2-pentylamine, water was azeotropically distilled with



$$H_2O + (CH_3)_2C{=}N{-}CH(CH_3)_2\ (V) \rightleftharpoons CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + CH_3{-}\overset{\overset{\displaystyle NH_2}{|}}{C}H{-}CH_3 \tag{8}$$

---

[7] E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, **10**, 242 (1951).

[8] The author is indebted to Professor Nathan Kornblum of Purdue University for an authentic sample of 2,4,4-trimethyl-2-nitropentane. In light of the work of Professor Kornblum and R. J. Clutter, *J. Am. Chem. Soc.* **76**, 4494 (1954), it is probably that the use of alkaline *tert*-butyl hydroperoxide at lower temperatures would give better conversions to nitroparaffins.

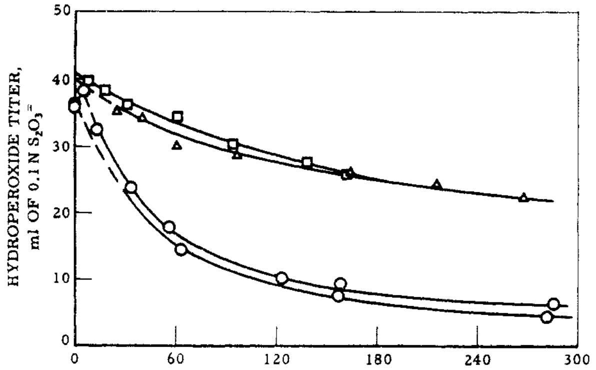


Fig. 4. Reduction of *tert*-butyl hydroperoxide by diisopropylamine. No additive (○), duplicate runs at $[RO_2H]_0 \approx 1.84M$, bath at 92.0 ± 0.2°C., kettle at 88 to 72°C; 1.8% 2,6-di-*t*-butyl-4-methylphenol (△), bath at 92.4 ± 0.6°C, kettle at 89 to 82°C; 2% Diphenylamine (□), bath at 91.9 ± 0.3°C and kettle at 88 to 82°C

tert-butyl alcohol during workup, and, therefore, it was possible to isolate good yields of I by fractional distillation of the crude. In the latter case, the equilibrium is also much more favorable to the ketimine side because the participating amine is present in large excess.

Functional group analyses (Table III) support the preceding arguments and give a quantitative measure of the products of the ketimine hydrolysis (8). The Van Slyke and carbonyl analyses were run under conditions in which V is essentially hydrolyzed to completion during or prior to analysis.

TABLE III

FUNCTIONAL GROUP ANALYSES. REACTION PRODUCTS FROM DIISOPROPYLAMINE AND *tert*-BUTYL HYDROPEROXIDE[a]

Analysis	Moles	Yield, %[b]
Hydroxyl value (*tert*-buytl alcohol)	0.17[c]	85
Carbonyl value (acetone)	0.187[d]	93
Primary amine (isopropylamine)	0.175[e]	88
Water	0.099[f]	45

[a] Kettle temperature, 92 to 73°; bath temperature, 92.2 ± 0.2°; amounts, (0.20 mole ROOH (91.7%w); 0.60 mole RNH_2; reaction time, 10 hr.; peroxide decomposed, 97%. [b] Moles of product/moles ROOH (100). [c] Corrected for *tert*-butyl alcohol content of the starting hydroperoxide. [d] Analysis was made on the distillate obtained by steam distillation of the acidified crude. [e] Analysis was made by the Van Slyke method on a separate run simulating the conditions used here. [f] Corrected for water content of the starting hydroperoxide. This indicates a $K_{equil.}$ value of roughly 1 for hydrolysis of the ketimine.

The rough overall rates of reduction of *tert*-butyl hydroperoxide by diisopropylamine were determined in the absence and presence of free radical inhibitors (Fig. 4). Clearly, the reaction is markedly inhibited by either diphenylamine or 2,6-di-*tert*-butyl-4-methylphenol. It is also seen that the hydroperoxide titer at ≤6 minutes shows a significant increase over and above the "t-zero" titer; this is more striking than shown because the "t-zero" value is not corrected for volume expansion on heating from room temperature to reaction temperature. This initial increase in titer is attributed to production of hydroperoxide by reaction of oxygen with radical intermediates prior to establishment of refluxing vapor, and correlates with the oxygen effect observed with 4-methyl-2-pentylamine (Fig. 2).

Isooctane extraction of the acidified reaction mixture inhibited with 2,6-di-*t*-butyl-4-methylphenol resulted in the isolation of IV, again indicating the capture of *tert*-butylperoxy radicals.

Tri-n-propylamine. The reduction of *tert*-butyl hydroperoxide by tri-*n*-propylamine (3:1 mole ratio) occurred as a fast exothermic reaction at 92°. In order to maintain equivalent bath and kettle temperatures, the reaction flask was removed and cooled shortly after immersion. The hydroperoxide was converted in good yield to the alcohol (see Table IV), and di-*n*-propylamine was isolated as the principal nitrogenous product. Although structural variations have not been studied at this time, this reaction appears promising as a device for degrading a tertiary amine to a secondary amine.[9] The group cleaved from the amine appears primarily as the corresponding aldehyde. Thus, the production of 2-methyl-2-pentenal is attributed to the condensation of propionaldehyde in the basic medium.

TABLE IV

PRODUCTS OF THE REACTION OF *tert*-BUTYL HYDROPEROXIDE WITH TRI-*n*-PROPYLAMINE[a]

Products	Moles	Yield %[c]
tert-Butyl alcohol	0.16	80
Water	[d]	—
Total carbonyl (principally 2-methyl-2-pentenal)	0.034[e]	17
Total "weak" acid (propionic + others)	0.002[f]	1
Di-*n*-propylamine	0.064	32
Recovered tri-*n*-propylamine	0.43	—
Unidentified (high boiling products)	(7.1 g)[g]	—

[a] Bath temperature, 82.4 ± 0.2°; kettle temperature,[b] 110 to 78.5°; amounts, 0.20 mole RO_2H, 0.61 mole RNH_2; reaction time, 3.5 hr.; peroxide decomposed, 100%. [b] Kettle temperature rose above bath temperature for a period of 5 to 10 minutes with flask out of bath. [c] Moles product/moles ROOH consumed (100). [d] No analysis was made. [e] This value was obtained by acidification of the crude mixture (another experiment) followed by steam distillation and analysis of the distillate. Isolation of the carbonyls as the 2,4 DNP's showed that there were present ≥91% 2-methyl-2-pentenal and ≤9% propionaldehyde. [f] See Table VI. [g] Part of this was shown to be basic and probably consists of amine coupling products; aldehyde condensate was also shown to be present. (See Experimental).

Infrared analysis showed the early appearance of a weak carbonyl band at ~5.78 μ (propionaldehyde) and the gradual development of a distinct and larger absorption peak at 5.89 μ (carbonyl

---

(9) Such a study has been reported with dibenzoyl peroxide; L. Horner and W. Kirmse, *Ann.*, **597**, 48 (1956).

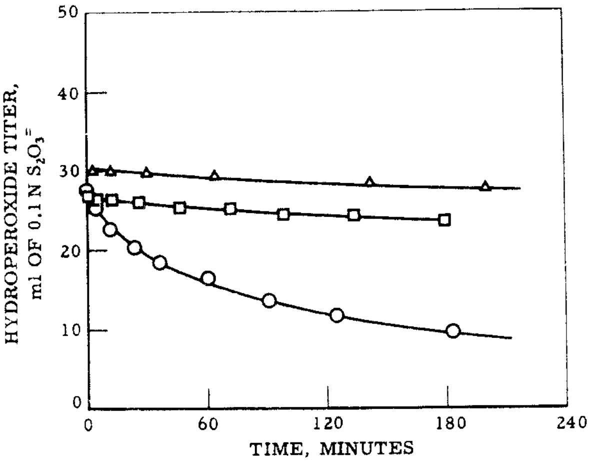


Fig. 5. Reduction of *tert*-butyl hydroperoxide with tri-*n*-propylamine. Bath at 60.4 ± 0.5°C, $[RO_2H]_0 \approx 1.5M$. Nitrogen flow (○), kettle at 63 to 56°C; 2% 2,6-di-*t*-butyl-4-methylphenol (□), kettle 60 ± 1°C; oxygen flow (△), kettle at 59 ± 1°C

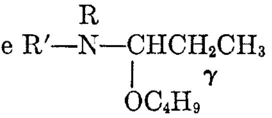
position in 2-methyl-2-pentenal). A weak but distinct peak was also observed at 6.02 μ; this suggested some imine formation but isolation work did not confirm this. As the C=C stretching absorption in 2-methyl-2-pentenal occurs at a ~6.08 μ in the pure aldehyde, the nature of the 6.02 μ component is not definitely established. The presence of water further obscures interpretation of the 6 μ region.

Kinetic experiments (Fig. 5) demonstrate the inhibitory effect of Ionol and *apparent* inhibitory effect of oxygen in the reduction of hydroperoxide by tri-*n*-propylamine. Isooctane extraction of a reaction mixture inhibited with 2,6-di-*tert*-butyl-4-methylphenol at 96% completion resulted in a recovery of 64 ± 10% of the original alkyl phenol plus 13% of the *tert*-butylperoxy-alkylphenol adduct (IV) (spectroscopic analysis). The conversion to IV is distinctly lower than that observed with primary and secondary amines reacted at only 40 to 50% completion (~50% yield of IV).

The *apparent* inhibition by oxygen is believed to be due to a hydroperoxide-forming reaction which is competitive with the normal reducing reactions of the amines, and may eliminate the chain character of the latter. When the tri-*n*-propylamine reaction is run under nitrogen, the ratio of amine consumed to peroxide destroyed is ~0.9 (see Table IV). The same reaction was carried out in the presence of oxygen and then hydrogenated after an apparent loss of twenty mmoles of hydroperoxide. Analysis of the hydrogenated mixture for tertiary amine showed a consumption of sixty-two mmoles or roughly three times the apparent hydroperoxide loss. Thus, in the presence of oxygen, amine is consumed by a competitive oxidation.

As direct distillation of the crude reaction mixture did not permit separation of the high boiling nitrogenous products from tri-*n*-propylamine, an attempt was made to do this by preliminary separation of the products into basic and nonbasic fractions utilizing extractive techniques. A summary of the data is presented in the Experimental section (see Table VII) for a reaction mixture containing initially *ca.* two moles of amine to one of hydroperoxide. The functional group data indicate that ~82% of the secondary amine formed is di-*n*-propylamine. Considering mechanical losses and analytical precision, it is probable that di-*n*-propylamine constitutes nearly all of the secondary amine formed. These data (Table VII) also suggest that some primary amine (~0.035 equiv.) is produced, but isolation work did not establish this. There was no indication of primary amine in the potentiometric titration curve obtained during the analysis of "secondary + tertiary" amine, and qualitative tests where also negative.

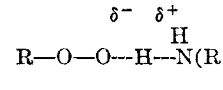
The amines boiling higher than tri-*n*-propylamine were difficult to separate as pure compounds; however, two constant boiling fractions were isolated. These fractions had compositions, respectively, of $C_{9.9}H_{20}N_{1.0}O_{1.0}$ (b.p. 98–99°/3 mm.) and $C_{12.8}H_{26}N_{1.0}O_{1.1}$ (b.p. 105–107°/2 mm.). Although not pure, it is plausible that these fractions contain structures of the type



$$R'\text{—}\overset{R}{N}\text{—}\underset{OC_4H_9}{\underset{|}{CH}}CH_2\overset{}{\underset{\gamma}{}}CH_3$$

(R′ = H and R = *n*-propyl in the first case and R = R′ = *n*-propyl in the second case), products expected from radical-radical association. Other high boiling basic N-containing substances may contain products of the type $(R_2N\text{—}CHR')_2$, but positive identification was not made. |

Amine-hydroperoxide complex formation. The mixing of any of the amines used in this investigation with *tert*-butyl hydroperoxide resulted, as expected, in a distinct but small evolution of heat. That the very weakly acidic *tert*-butyl hydroperoxide forms a complex with an aliphatic amine is readily demonstrated by comparison of infrared spectra of dilute solutions of hydroperoxide with hydroperoxide-amine solutions. The shift in the O—H stretching band as seen in *Table V* is that expected for hydrogen-bonded complex formation of the type:



$$R\text{—}\overset{\delta^-}{O}\text{—}O\text{---}\overset{\delta^+}{H}\text{---}\overset{H}{N}(R)_2.$$

Diisopropylamine was chosen to demonstrate this point because the pure amine shows virtually no N—H stretching absorption in a 0.012 mm. cell (two peaks at 3.02 and 3.14 μ are just discernible) and, therefore, the 3 μ region is more easily interpreted. Although the other amine-hydroperoxide systems were not investigated in such detail, examination of crude reaction mixtures at

TABLE V

DIISOPROPYLAMINE-*tert*-BUTYL HYDROPEROXIDE. INFRARED EVIDENCE FOR COMPLEX FORMATION IN CARBON TETRACHLORIDE[a]

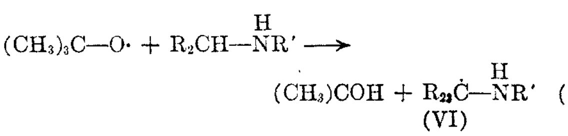
$[RNH_2]$ M./L.	$[ROOH]$[b] M./L.	Remarks
1.01	1.02	Principal O—H stretching at 3.22 μ; shoulders at 3.06 and 2.81 μ (trace).
—	1.02	Principal O—H stretching at 2.94 μ; shoulder at 2.81 μ.
—	0.20	Increased intensity (sharp band) at 2.81 μ (unbonded OH); broad band at 2.93 μ (bonded OH).

[a] 0.109 Mm. cell. [b] Prepared from a 91.7%w stock of RO_2H.

low peroxide consumption suggested that these exhibit similar shifts in the OH region.

Reaction of di-tert-butyl peroxide with aliphatic amines. Earlier work from This Laboratory established that the decomposition of di-*tert*-butyl peroxide in tri-*n*-butylamine gave nearly quantitative yields of *tert*-butyl alcohol.[10] It was of interest in this present study to determine the behavior of *tert*-butoxy radicals in the presence of a primary and secondary amine as well. The results in Table VI show that the amines studied are all good hydrogen donors with a rough order of activity: tertiary ≈ secondary > primary. Although no attempt was made to isolate the products, gas-liquid partition chromatography, infrared spectra and functional group analyses (see Table VI) indicated that the principal hydrogen donating processes are 10 and 11, particularly with diisopropylamine.[11] Disproportionation and dimerization of the intermediate radical (VI) are also expected to occur; the latter appears to be more important with 4-methyl-2-pentylamine.

$$\mathrm{(CH_3)_3C{-}O{-}O{-}C(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot} \qquad (9)$$



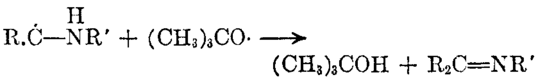
$$\mathrm{(CH_3)_3C{-}O\cdot + R_2CH{-}\overset{H}{N}R' \longrightarrow (CH_3)COH + \underset{(VI)}{R_2\dot{C}{-}\overset{H}{N}R'}} \qquad (10)$$

TABLE VI

DECOMPOSITION OF DI-*tert*-BUTYL PEROXIDE IN ALIPHATIC AMINES[a]

Amine	Moles/50 Moles of Peroxide		Moles/100 Moles of Peroxide, —C=N—Production
	tert-Butyl Alcohol	Acetone	
Tri-*n*-butyl[b]	~95	~5	...
Diisopropyl	95[c]	≦5[d]	≧81[e]
4-Methyl-2-pentyl	87[c]	≦13[d,f]	≧53[e]

[a] $[\text{Peroxide}]_0$, 0.86 to 0.90 moles/kg. of solution; temperature, 130.5° ± 0.5°; time, 24 hr. (*ca.* 4.5 half-lives). [b] See ref. 10. [c] The crude reaction mixtures were acidified and steam distilled; hydroxyl values and total carbonyl values were determined on the distillate. [d] These values were estimated by the difference between the hydroxyl value found and the theoretical value based on complete decomposition of the peroxide. GLC analysis indicated that only traces of peroxide remained. [e] These values were arrived at by correcting the total carbonyl value of the steam distillates downward by the maximum acetone yield indicated in column 3. It was assumed that the hydrolysis of the ketimine is complete during the analysis ($R_2C = NR + H_2O \longrightarrow R_2C = O + RNH_2$). [f] Gas phase chromatography and infrared analysis indicated that there was essentially no acetone present at time of analysis. Assuming that acetone reacts only with amine to form ketimine and water, then the water content should be an alternative measure of acetone production. Water analysis of the crude gave values of 8 and 62 in columns 3 and 4.



$$\mathrm{R.\dot{C}{-}\overset{H}{N}R' + (CH_3)_3CO\cdot \longrightarrow (CH_3)_3COH + R_2C{=}NR'} \qquad (11)$$

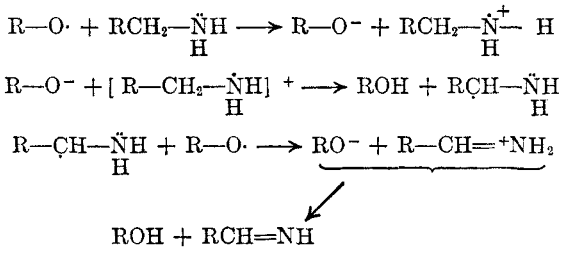
It is clear that aliphatic amines bearing *alpha* hydrogen atoms are excellent hydrogen donors for *tert*-butoxy radicals.[12]

---

(10) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

(11) The N—H bond strength in ammonia is reported as 100–104 kcals.; however, the N—H bond dissociation energy of the amines used in this study is still uncertain. Nevertheless, it is probable that the energy of the C—H bond *alpha* to nitrogen is substantially less than the secondary C—H in propane (89–94 kcals.) and less than the N—H bond in an amine (see T. L. Cottrell, *The Strength of Chemical bonds*, Academic Press, Inc., N. Y., N. Y., 1954, pp. 187, 188, 192 for quoted values). The recent work of W. H. Urry and O. O. Juveland, *J. Am. Chem. Soc.*, **80**, 3233 (1958) likewise supports α-carbon-hydrogen attack by free radicals. Therefore, hydrogen abstraction directly from nitrogen seems unlikely.[12] The reactivity of the *alpha* C—H in alcohols towards radical attack (A. V. Tobolsky, R. B. Mesrobian, *Organic Peroxides*, Interscience Publishers, Inc., New York, N. Y., 1954, p. 84) is also consistent with this argument.

(12) It is possible that R—O· radicals do not abstract hydrogen directly, but react first by electron exchange:



$$\mathrm{R{-}O\cdot + RCH_2{-}\underset{H}{\ddot{N}}H \longrightarrow R{-}O^- + RCH_2{-}\underset{H}{\overset{\cdot +}{N}}{-}\ H}$$

$$\mathrm{R{-}O^- + [R{-}CH_2{-}\underset{H}{\dot{N}}H]^+ \longrightarrow ROH + R\underset{\cdot}{C}H{-}\underset{H}{\ddot{N}}H}$$

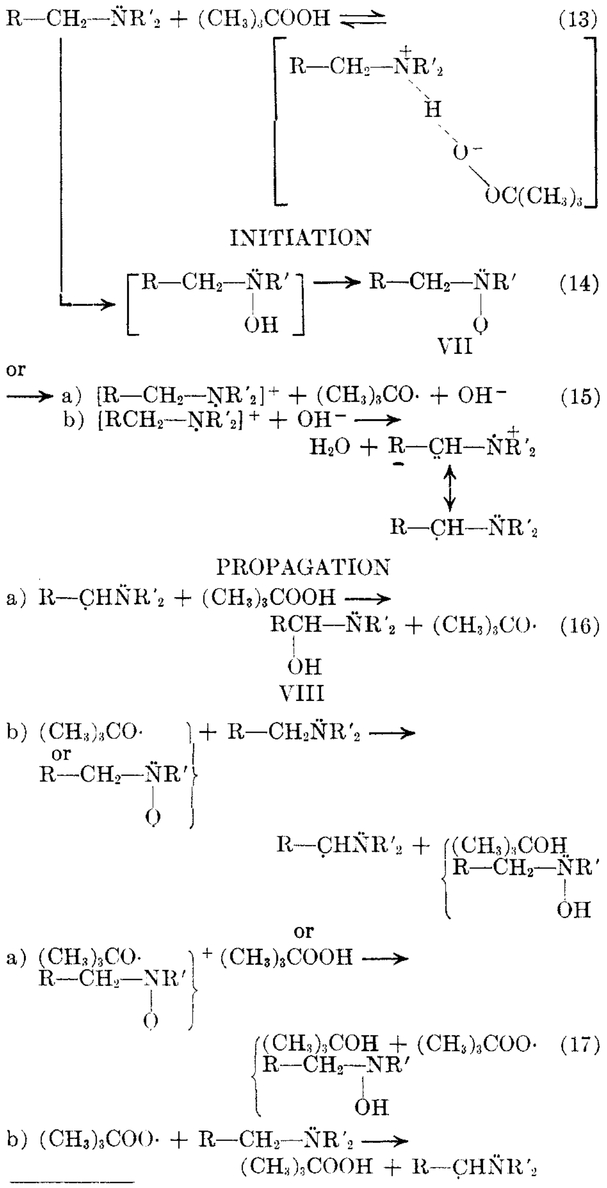
$$\mathrm{R{-}\underset{\cdot}{C}H{-}\underset{H}{\ddot{N}}H + R{-}O\cdot \longrightarrow \underbrace{RO^- + R{-}CH{=}{}^+NH_2}}$$

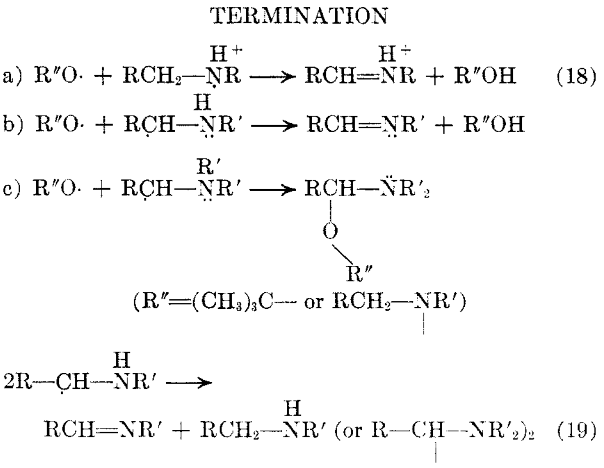
$$\mathrm{\swarrow}$$

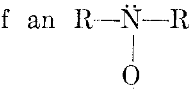
$$\mathrm{ROH + RCH{=}NH}$$

Without further experimental work, it becomes impossible rigidly to exclude this path. In this respect, 2,4,4-trimethyl-2-pentylamine (unpublished work from this laboratory) has recently been shown to be a relatively good hydrogen donor (~80% yield of *tert*-butyl alcohol at 136°). It is a much better donor than isooctane, its hydrocarbon analog. The *tert*-butyl alcohol to acetone ratio in the former case at 135° was ~1.6 (data kindly furnished by Dr. J. H. Raley of this laboratory) while the ratio with *tert*-octylamine is ≧4.3 at 136°. The "donation process" may, of course, be a case of direct hydrogen atom abstraction from nitrogen, as this amine has no *alpha* hydrogens. Unfortunately, the "donation process" is accompanied by a rather substantial tar formation from the amine moiety and isolation work has not as yet been successful in elucidating the course of the reaction.

Mechanism. Major reaction. A precise kinetic analysis of the aliphatic amine–hydroperoxide reaction has not been made. Indeed, such a study would require conditions leading to a more clean-cut stoichiometry, or the use of initial rate techniques to avoid the complication of secondary processes. Inhibition by typical free radical traps such as 2,6-di-*tert*-butyl-4-methylphenol and diphenylamine, apparent inhibition by oxygen, and the marked acceleration of hydroperoxide decomposition[13] in amine solvents are consistent with the following mechanism:



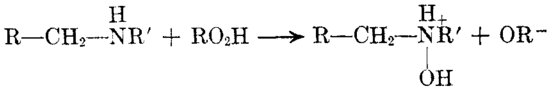


Complex formation (13) is substantiated by infrared measurements. The one electron transfer from amine to peroxide (15) and production of the oxy radical VII (14) probably occur through formation of an unstable quaternary ammonium salt as proposed by Walling for acyl peroxide–amine systems[14b] and other workers for decomposition of *N*-haloammonium ions.[14c] Since the termination of this chemical investigation, Drs. G. M. Coppinger and J. D. Swalen[14d] of this laboratory have made available to the author some physical studies which provide direct evidence for a previously unrecognized radical (VII), and suggest quaternary-salt formation as an intermediate. These workers have examined a large number of aliphatic (*tert*- and *sec*-) amine–*tert*-butyl hydroperoxide systems by the electron magnetic resonance technique. In every case examined, a strong radical spectrum characteristic of an  $\mathrm{R}-\underset{\underset{\mathrm{O}}{|}}{\ddot{\mathrm{N}}}-\mathrm{R}$ species was observed. Although other radicals could have been present and gone undetected because of their lower steady state concentration, it is striking that the $R_2NO\cdot$ species attained a steady state concentration as high as $10^{-3}M$. Clearly, such a radical must be an important species in the mechanism of hydroperoxide-amine interaction. However, when these reactions are carried out in *excess* amine, the likely successor of such a radical, R_2N—OH, is not isolated. First, it is apparent that material balances are not good enough to establish the absence of hydroxylamines or their successors in the current work, although they are clearly not major products. Second, unpublished work by G. M. Coppinger and the author has now established that dibenzylhydroxylamine is rapidly oxidized by *tert*-butyl hydroperoxide in an inert (benzene) solvent. The oxidation of the hydroxylamine also exhibits the electron magnetic resonance spectrum of R_2N—O·. These facts suggest that the R_2N—O· species functions principally as a propagating radical.

---

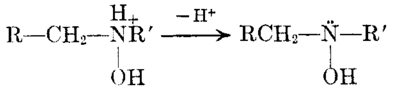
[13] Control experiments utilizing *n*-octane solutions of hydroperoxide (80–90% purity in this investigation, and high purity in an earlier investigation from this laboratory, see ref. 7) have demonstrated that the thermal decomposition of *tert*-butyl hydroperoxide at 1 to 2*M* in hydrocarbon is very slow at or below 110°. Clearly, such a process must make a relatively minor contribution to the overall oxidation of amines bearing *alpha* hydrogen atoms. See also recent work by B. Kathleen Morse, *J. Am. Chem. Soc.*, **79**, 3310 (1957).

Oxidation of a secondary amine could be rationalized in the following manner:

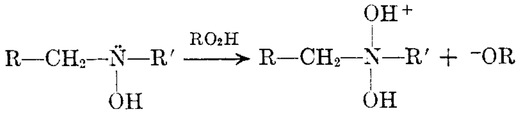


$$R{-}CH_2{-}\overset{H}{N}R' + RO_2H \longrightarrow R{-}CH_2{-}\overset{H_+}{\underset{OH}{N}}R' + OR^- \qquad (20)$$

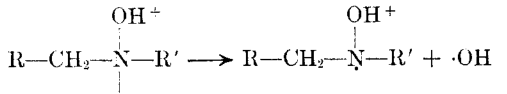
(R' = H or alkyl)



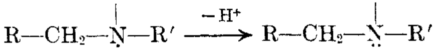
$$R{-}CH_2{-}\overset{H_+}{\underset{OH}{N}}R' \xrightarrow{-H^+} RCH_2{-}\underset{OH}{\ddot{N}}{-}R' \qquad (21)$$



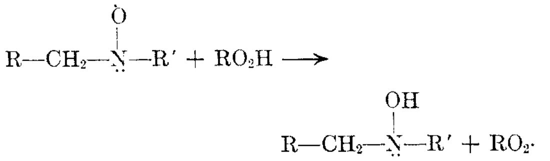
$$R{-}CH_2{-}\underset{OH}{\ddot{N}}{-}R' \xrightarrow{RO_2H} R{-}CH_2{-}\overset{OH^+}{\underset{OH}{\dot{N}}}{-}R' + {}^-OR \qquad (22)$$



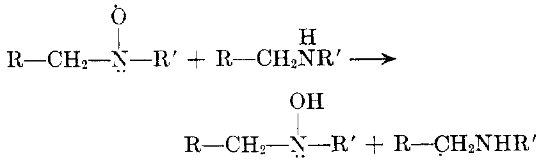
$$R{-}CH_2{-}\overset{OH^+}{\underset{OH}{\dot{N}}}{-}R' \longrightarrow R{-}CH_2{-}\overset{OH^+}{\dot{N}}{-}R' + \cdot OH \qquad (23)$$



$$R{-}CH_2{-}\overset{OH^+}{\dot{N}}{-}R' \xrightarrow{-H^+} R{-}CH_2{-}\overset{\dot{O}}{\dot{N}}{-}R' \qquad (24)$$



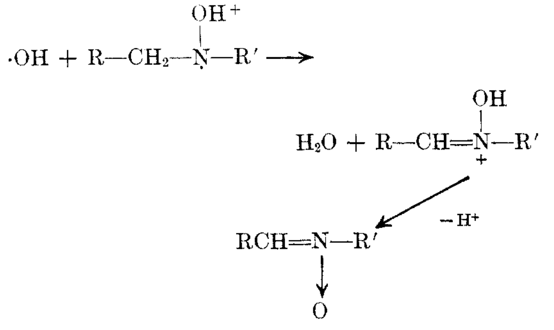
$$R{-}CH_2{-}\overset{\dot{O}}{\dot{N}}{-}R' + RO_2H \longrightarrow R{-}CH_2{-}\overset{OH}{\dot{N}}{-}R' + RO_2\cdot \qquad (25)$$



$$R{-}CH_2{-}\overset{\dot{O}}{\dot{N}}{-}R' + R{-}CH_2\overset{H}{N}R' \longrightarrow R{-}CH_2{-}\overset{OH}{\dot{N}}{-}R' + R{-}\underset{\cdot}{C}H_2NHR' \qquad (26)$$

$$R{-}\underset{\cdot}{C}H{-}NHR' + \cdot OH \text{ (or other R}\cdot) \longrightarrow R{-}CH{=}NR' + H_2O$$

This scheme would predict the regeneration of the hydroxylamine except where its radical precursor is terminated by a radical-radical reaction, *e.g.*:



$$\cdot OH + R{-}CH_2{-}\overset{OH^+}{\dot{N}}{-}R' \longrightarrow H_2O + R{-}CH{=}\overset{OH}{\underset{+}{N}}{-}R' \qquad (27)$$

$$\xrightarrow{-H^+} RCH{=}\underset{\substack{\downarrow\\ O}}{N}{-}R'$$

Thus, the hypothesis is that the hydroxylamine and its radical precursor are readily interconvertable. Preliminary data (unpublished) indicate that the nitrone is formed in good yield by hydroperoxide attack on dibenzylhydroxylamine in dilute benzene solution. However, in *excess* amine this reaction is minimized. The cleavage step (23) is consistent with the recently reported radical chain decomposition of *N*-haloammonium ions.[14c]

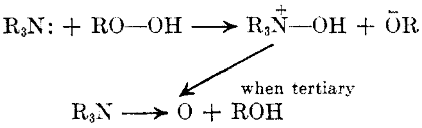
No radical spectrum has been observed in the case of the primary amine, although by analogy it would be expected to follow the pattern of the secondary amine. One can conclude at this stage only that the concentration of any intermediate radical is not sufficiently high to detect by the electron magnetic resonance technique.

The rationalization of an $R_2N{-}O\cdot$ species in the *tert*-amine case (e.g., tri-*n*-propyl) is not straightforward, although presumably it arises to some extent from the di-*n*-propylamine formed in the reaction. Further work is needed to establish the initiation step of this reaction. By analogy with the secondary amine, the amine oxide might be expected as a primary intermediate which would give dipropylhydroxylamine and propylene by the usual elimination path. Evidence for the latter was not obtained in this investigation, but the electron magnetic resonance evidence suggests a re-examination of this system. Without further work, step (15) cannot be excluded as an alternative mode of initiation in the *tert*-amine-peroxide system. This one-electron transfer to the O—O bond is analogous to the process proposed by Horner for the reaction of dialkyl anilines with benzoyl peroxide.[14a] Proton loss (15) from the aminium radical produces water and the corresponding α-carbon radical[14a,15]. The formation

---

(14) (a) See L. Horner and H. Junkerman, *Ann.*, **591**, 53 (1955) and earlier references cited therein.

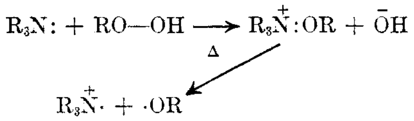
(b) For an excellent summary of amine-peroxide chemistry, see C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 590–595; C. Walling and N. Indictor, *J. Am. Chem. Soc.*, **80**, 5814 (1958). It seems reasonable to write the initial step (Equation 14) in this mechanism as an amine displacement on the peroxide bond:



$$R_3N{:} + RO{-}OH \longrightarrow R_3\overset{+}{N}{-}OH + \bar{O}R$$

$$\xrightarrow{\text{when tertiary}} R_3N \longrightarrow O + ROH$$

However, with the tertiary amine this should give rise to amine oxide. No direct evidence has been obtained for the latter or its degradation products. Alternatively, electron transfer may occur by:



$$R_3N{:} + RO{-}OH \longrightarrow R_3\overset{+}{N}{:}OR + \bar{O}H$$

$$\xrightarrow{\Delta} R_3\overset{+}{N}\cdot + \cdot OR$$

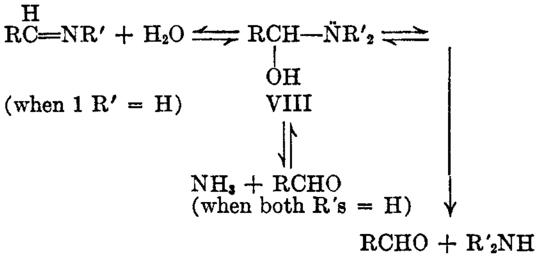
(c) E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **80**, 2903 (1958). W. R. Hertler, Doctoral Dissertation, Dissertation Abstracts, University Microfilms Inc., Ann Arbor, Michigan, Vol. XIX, 1958, p. 956. P. Buchschacher, J. Kalroda, D. Arigoni, and O. Jeger, *J. Am. Chem. Soc.*, **80**, 2905 (1958). S. Wazonek and T. P. Culbertson, 135th Meeting of the American Chemical Society, Boston, Mass., April 1959, Abstracts of Papers, p. 42–0.

(d) The author is deeply indebted to Drs. Coppinger and Swalen for permission to use these data in advance of their forthcoming publication.

(15) Proton loss from nitrogen (Equation 15 where R' = H) would lead to a nitrogen radical which could equally well participate. However, we have isolated no products which are derivable from this source although their presence cannot be excluded.

of a positive nitrogen radical (aminium radical) is by no means a new concept. In the case of some aryl and alkyl aryl amines, stable aminium salts have been prepared.[16]

The displacement of a radical on the O—O bond (16-a) is without good analogy in liquid phase *hydroperoxide* work. However, an analogous intramolecular process has been proposed in the vapor phase oxidation of isooctane[17] and in the liquid phase decomposition of pure di-*tert*-butyl peroxide and di-*tert*-heptyl peroxide.[18] An example of radical displacement on the O—O bond of benzoyl peroxide has recently received strong experimental support.[18c,d] The reaction is not inconsistent with the retardation caused by typical inhibitors and gives an intermediate (VIII) which leads to the expected products:



$$\begin{array}{l}\mathrm{R\overset{H}{C}{=}NR' + H_2O \rightleftharpoons R\underset{\substack{|\\ OH}}{C}H{-}\ddot{N}R'_2 \rightleftharpoons}\\ (\text{when 1 R}' = \text{H}) \qquad \mathrm{VIII}\\ \qquad\qquad\qquad \rightleftharpoons\\ \qquad \mathrm{NH_3 + RCHO}\\ \qquad (\text{when both R's} = \text{H})\\ \qquad\qquad\qquad\qquad \mathrm{RCHO + R'_2NH}\end{array}$$

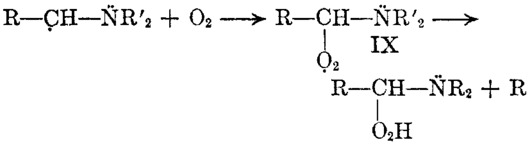
(28)

The chain transfer step (17a) explains the capture of *tert*-butylperoxy radicals by 2,6-di-*tert*-butyl-4-methylphenol, and receives support from earlier work which showed that *tert*-butyl hydroperoxide is subject to induced decomposition through abstraction of the hydrogen bound to oxygen.[7] The previously cited observations on the decomposition of di-*tert*-butyl peroxide in amines are also consistent with hydrogen abstraction by oxy radicals (Equation 16-b) leading to *alpha*-amino radicals and hence to ketimine-type products. In the case of primary and secondary amines, the aminium radicals or *alpha*-amino radicals may give rise directly to ketimine products by termination steps 18a, 18b, or 19.[19]

Certainly there is good evidence for free radical participation in these amine-hydroperoxide reactions. However, our data do not preclude the participation of ionic processes other than those already suggested. Solvent effects and poor initiating efficiency[14b] in some amine–acyl peroxide systems suggest that ionic processes may be occurring concomitantly in the hydroperoxide-amine systems.[20]

The current results are in qualitative agreement with Hawkins'[1] observation that the reaction rate of hydroperoxide with simple monoamines follows the sequence: primary<secondary<tertiary. It is clearly not simply a matter of base strength toward a proton acid (complex formation, Equation 13), as this would follow the relative rate order: tertiary<primary<secondary. However, in lieu of precise determination of the kinetics, and knowledge of the rate determining step, it appears unwise to elaborate on this difference.

Inhibition. The *apparent inhibition* of these amine-hydroperoxide reactions by oxygen is attributed to the interaction of *alpha*-amino radicals with oxygen, presumably a hydroperoxide producing reaction[21]: Bickel and Kooyman[22] have



$$\begin{array}{l}\mathrm{R{-}\underset{\cdot}{C}H{-}\ddot{N}R'_2 + O_2 \longrightarrow R{-}\underset{\substack{|\\ O_2}}{C}H{-}\ddot{N}R'_2 \longrightarrow}\ \mathrm{IX}\\ \qquad\qquad\qquad \mathrm{R{-}\underset{\substack{|\\ O_2H}}{C}H{-}\ddot{N}R_2 + R\cdot}\end{array}$$

(29)

recently observed that some tertiary alkyl aromatic amines in autoxidation systems do indeed produce radicals which are capable of adding oxygen.

With respect to inhibition by 2,6-di-*tert*-butyl-4-methyl or other phenols, primary and secondary amines appear to give a much better yield of the

---

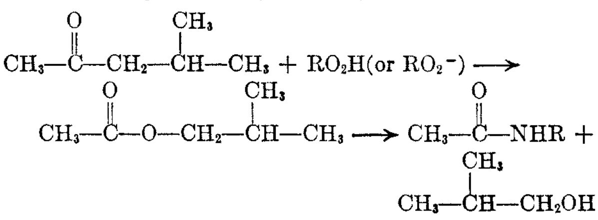
(16) See V. Franzen, *Ber.*, **88,** 1697 (1955) and R. I. Walter, *J. Am. Chem. Soc.*, **77,** 5999 (1956).

(17) F. F. Rust and D. O. Collamer, Jr., *J. Am. Chem. Soc.*, **76,** 1055 (1954).

(18) (a) E. R. Bell, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **72,** 337 (1950). (b) H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **81,** 2691 (1959). (c) E. H. Drew and C. H. Martin, *Chem. and Ind.*, 925 (1958). (d) D. B. Denney and G. Feig, *J. Am. Chem. Soc.*, **81,** 5323 (1959).

(19) Termination 18-a gives ketimine directly by proton loss from nitrogen. With tertiary amine, this step followed by proton loss from "β-carbon" gives "enamine." Hydrolysis of the latter would give the observed products. Walling and Indictor (*loc. cit.*) and D. Buckley, S. Dunstan, and H. B. Henbest, *J. Chem. Soc.*, 4901 (1957), have observed enamine formation in the reaction of benzoyl peroxide with triethyl amine.

(20) In the slower oxidation reactions of amines by hydroperoxide (*e.g.*, 4-methyl-2-pentyl and primary amines in general; see Experimental) the hydroperoxide may become involved in secondary reactions of the Baeyer-Villiger type (see J. E. Leffler, *Chem. Rev.*, **45,** 385 (1949) and C. H. Hassall, *Org. Reactions*, 74 (1957).



$$\begin{array}{l}\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3 + RO_2H(or\ RO_2^-) \longrightarrow}\\ \mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3 \longrightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}NHR +}\\ \qquad\qquad\qquad\qquad\qquad\qquad \mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_2OH}\end{array}$$

The isolation of bis-*N,N'*-(4-methyl-2-pentyl)oxalamide (Table I) was indeed surprising. It is difficult to picture its formation except by a circuitous route involving the formation of *N*-(4-methyl-2-pentyl)formamide, subsequent abstraction of the formyl hydrogen and dimerization of the resultant radical. It is also conceivable that hydroperoxide may attack ketimines to give oxazirane intermediates. This phase of hydroperoxide-amine chemistry remains to be explored further.

(21) In theory, it should be possible to trap the amino peroxy radicals (IX) with 2,6-di-*tert*-butyl-4-methylphenol; however, our method of isolation of the adducts of $RO_2\cdot$ with 2,6-di-*tert*-butyl-4-methylphenol (*e.g.* IV) would have presumably precluded isolation of the adduct of IX because of its solubility in dilute hydrochloric acid.

(22) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2220 (1957).

tert-butylperoxy-alkylphenol adduct (IV) than, *e.g.*, tri-*n*-propylamine at even greater conversion. As all of the amines are very good hydrogen donors, this finding would not appear to be solely a result of the difference in rate of the respective hydrogen abstraction processes (16-b). It may well reflect the longer chain lengths involved in hydroperoxide–tertiary amine reactions; in the latter system, the *alpha*-amino radicals are not subject to termination step 18-b and 19 which necessitate having a hydrogen bound to nitrogen.[20] Alternatively, this observation may be due to varying degrees of competition by ionic paths.

EXPERIMENTAL

Materials. The amines were purified by fractionation in a 100-cm. helices-packed column prior to use. The source and physical properties are: 4-methyl-2-pentylamine (b.p. 108°, n_{D}^{20} 1.4081)[23], 2,4,4-trimethyl-2-pentylamine (Rohm and Haas; b.p. 139.5–140°, n_{D}^{20} 1.4237), diisopropylamine (Eastman Kodak; b.p. 83.5–84°, n_{D}^{20} 1.3917 to 1.3920) and tri-*n*-propylamine (Eastman Kodak; b.p. 156–156.5°, n_{D}^{20} 1.4161).

The *tert*-butyl hydroperoxide was obtained from the Lucidol Corporation. It was steam distilled to remove the di-*tert*-butyl peroxide until the head temperature reached ~91°. At this point the organic layer in the kettle was separated from the aqueous layer and then fractionated *in vacuo*, maintaining a kettle temperature <40°. Fractions analyzing (iodometrically) ~78–94%w hydroperoxide were used in the current work. Each stock was analyzed separately for hydroperoxide and water, and the balance was assigned on the basis of infrared evidence to *tert*-butyl alcohol; analyses of some typical peroxide stocks were 82.0, 87.8, 91.7, and 94.1% hydroperoxide, and 0.51, 0.45, 1.35, 0.2% water, respectively. Hydrogenation (platinum at room temperature) of the 82.0% stock followed by functional group analysis gave a value consistent with the estimated *tert*-butyl alcohol content of 17.5%.

Di-*tert*-butyl peroxide (Shell Chemical Corp.) was used without further purification. All other organic chemicals were for the most part Eastman Kodak white-label products and were used without further purification.

General procedure. The reactions were usually run in excess amine (roughly 3 RNH_2:1 ROOH) and unless noted no attempt was made to exclude oxygen since the conditions were usually such that reflux conditions were soon established. However, in the rough kinetic experiments with tri-*n*-propylamine, the system was swept with nitrogen. The reaction flask was usually a two necked flask of suitable volume equipped with a small sampling condenser and an efficient coil condenser; the latter was in turn connected to a Dry Ice trap, and a gas collection bottle if gases were to be determined. Zero time was taken as time of immersion in the bath.

Peroxide analyses were made by withdrawing samples and quenching by pipetting into cold isopropyl alcohol (50 ml.) containing 5 ml. of glacial acetic acid, ≦ 1 ml.[24] of 6*N* hydrochloric acid and 2 ml. of saturated sodium iodide; a small piece of Dry Ice was added directly to the solution before the sample was introduced. After refluxing for 5 min. under a carbon dioxide atmosphere, the liberated iodine was titrated with 0.1*N* thiosulfate.

The reaction products were separated by distillation through a 20-cm. helices-packed column and/or an efficient Piros-Glover spinning band column depending on the ease of separation. The crude reaction mixtures were also examined by infrared analysis (see results) during the course of the reaction.

Isolation of inhibitor products. The inhibited reactions were acidified and extracted with isooctane. The extract was washed and concentrated, and infrared and/or ultraviolet spectra obtained on the concentrate.

In the isolation work on 4-methyl-2-pentylamine, a crystalline product, m.p. 85.5–86.5°, was obtained by recrystallizing the solid residue remaining after evaporation of the isooctane. This material showed no depression in melting point on mixing with authentic IV. The infrared spectrum of the isooctane extract was compatible with the authentic spectrum of IV, and the ultraviolet spectrum showed the characteristic absorption of the cyclohexadienone structure at ~233 mμ[5]. Similar evidence was obtained for the production of IV in the inhibited reaction of diisopropylamine. In the case of the tri-*n*-propylamine, an attempt to purify the crude residue by chromatography and recrystallization gave an impure product, m.p. 49 to 53° (cloudy melt). That this mixture contained IV was easily demonstrated by infrared analysis.

Analytical methods. The functional group analyses employed were standard methods of this laboratory. Water was determined by titration with the Fischer reagent. Hydroxyl values (tertiary) were determined by esterification in the presence of boron trifluoride followed by a Fischer water determination. Carbonyl values were determined by reaction with hydroxylamine followed by determination of the water formed, or by an aqueous method using hydroxylamine hydrochloride and titrating the hydrogen chloride liberated in the reaction. Secondary plus tertiary amine values were obtained by conversion of the primary amine to an azomethine or Schiff's base followed by potentiometric titration for the former. Basic nitrogen values were obtained by electrometric titrations (perchloric acid in acetic acid titrant). Primary amine, in the case of isopropylamine, was determined by a conventional Van Slyke method.

Gases were usually determined by mass spectrometric methods. Ammonia (*Table I*) was condensed in a Dry Ice trap and then distilled into a known volume of water. An aliquot of the latter solution was titrated with standard acid.

Isolation and identification of products from 4-methyl-2-pentylamine. After distillation of a crude reaction mixture from a typical experiment (see *Table I*) in a 20-cm. helices-packed column, the following fractions were obtained (boiling point at atmospheric pressure unless noted):

Fraction 1 (b.p. 79–83.7, n_{D}^{20} 1.3878, 20.3 g.) was shown to contain *tert*-butyl alcohol (hydroxyl value 1.07 eq./100 g.) and water (15.3%w). Identification was based on the physical constants (lit. value for water–*tert*-butyl alcohol azeotrope: b.p. 79.9°, 11.76% H_2O)[25] and infrared analysis.

Fraction 2 (b.p. 84–107°, n_{D}^{20} 1.4029, 11.8 g.) contained *tert*-butyl alcohol (hydroxyl value 0.626 eq./100 g.), water (2.8%w), and 4-methyl-2-pentylamine (0.0648 eq. total by titration with standard acid). Fractions 3 and 4 (b.p. 107.5–108° and 35–37°/48 mm., n_{D}^{20} 1.4079, 29.6 g.) contained recovered 4-methyl-2-pentylamine.

Fraction 5 (b.p. 73–77°/48 mm., n_{D}^{20} 1.4288, 1.4 g.) was estimated as 89%w I and 11% 4-methyl-2-pentylamine on the basis of refractive index. *N*-(4-methyl-2-pentylidene)-4-methyl-2-pentylamine, I, was isolated in fractions 6 to 9 (b.p. 77–78°/48 mm. and 44–49°/3 mm., n_{D}^{20} 1.4313 to 1.4305, 25.5 g.); lit.[26] values: b.p. 128.8°/100 mm., n_{D}^{20}

---

[23] The author is indebted to D. G. Norton of this laboratory for a generous supply of this material.

[24] Mineral acid (hydrochloric acid) was usually added in an amount slightly in excess of the amine present in the sample; however, later analyses in which the hydrochloric acid was omitted were in good agreement with those done in its presence.

[25] L. H. Horsley, *Azeotropic Data*, American Chemical Society Monograph, Washington, D. C., 1952, p. 8.

1.4313). The infrared spectrum was identical with an authentic spectrum (strong —C═N— band at 6.01 μ).

The column holdup (1.7 g., n_D^{20} 1.4479) showed characteristic infrared bands at 3.03 μ (moderately strong; shoulder at 3.24), ~6.03 (strong) and 6.43 (strong) which suggested the possibility of an *N*-monosubstituted amide. Further work was done on similar high boiling material from a larger scale run (1.02 moles of hydroperoxide and 2.04 moles of amine at 110°). This latter material was distilled through the spinning band column and two predominant high-boiling cuts were collected and examined. Fractions 3 to 6 (b.p. 101–105°/4 mm., n_D^{20} 1.4473–1.4482, 12.6 g.) showed the infrared pattern described for the column holdup.

Anal. Found: C, 77.4; H, 13.0; Basic N, 2.8; N, 7.2.

Fractions 8 to 9 (b.p. 114–118°/4 mm., n_D^{20} 1.4521–1.4525, 5.8 g.) had an infrared spectrum remarkably similar to fractions 3 to 6 with the exception that the intensity of the 6.04 μ band was decreased slightly and that of the 6.43 band was substantially decreased (less amide).

Anal. Found: C, 79.0; H, 13.2; Basic N, 4.2; N, 5.99.

These fractions were partially resolved by chemical methods. Acidic hydrolysis of fractions (3) to (6) followed by steam distillation resulted in the isolation of acetic acid as the *p*-bromophenacyl acetate (m.p. 83.2–83.7°; mixed m.p. with authentic sample 83.6–84.6°) and the *p*-phenylphenacyl acetate (m.p. 108.5–110°; lit. value 111°). However, the isolation work indicated that another acid was probably present but efforts to purify other fractions of the solid esters failed. The steam distillate also contained a small amount of water-insoluble material whose infrared spectrum (carbon tetrachloride extract) indicated the presence of α,β-unsaturated ketone. Treatment of the extract with acidic 2,4-dinitrophenylhydrazine reagent gave a crude 2,4-dinitrophenylhydrazone which contained five components (chromatographic analysis); the melting point of the major component, m.p. 81–82°, was not depressed on mixing with authentic 2,4-dinitrophenylhydrazone (83–84°) from methyl isobutyl ketone.

When the acidic hydrolysis mixture was made basic (pH ≥11), 4-methyl-2-pentylamine was liberated and isolated as the phenylthiourea, m.p. 108.5–109.5° (not depressed with authentic sample).

An aliquot of fractions (8) and (9) was reduced with hydrogen over platinum at room temperature, absorbing hydrogen equivalent to ~1 mole uptake/187 g. An attempt to isolate a derivative from the reduced product failed; however, the infrared spectrum indicated a substantial decrease in intensity at the 6.05 μ position with little or no change in the 6.4 μ band.

The above mentioned facts and the elemental and infrared analyses suggest that fractions 3–6 and 8–9 probably consist of a basic component (possibly a ketimine arising from aldol-type condensation of I) and one or more nonbasic components (probably *N*-(4-methyl-2-pentyl)acetamide and other amides). It is clear from the elemental analyses that the *N*-substituted acetamide could not be the only amide present assuming that the basic material is the ketimine condensate of I.[27] The presence of the *N*-substituted isovaleroamide would be in reasonable agreement with the data assuming ketimine condensate to be present in fractions 3–6 and 8–9.

The kettle residue (2.1 g., partly crystalline) was not further examined. However, with similar material from another experiment, a crystalline solid (~1.5 g. from 1.0 mole of ROOH) was isolated and recrystallized from petroleum ether (b.p. 30–60°), m.p. 132.5–134° (probably melts with decomposition; a clear melt is not obtained). Infrared analysis and NMR spectroscopy, along with the elemental analysis, suggested that the structure was *N*, *N'*-bis(4-methyl-2-pentyl)oxalamide; this was confirmed by synthesis of the latter, m.p. 132.5–134° (see above). Mixed melting point showed no depression and infrared spectra of the unknown and known were identical.

Anal. Calcd. for $C_{14}H_{28}N_2O_2$: C, 65.6; H, 11.0; N, 10.9; molecular weight 256.4. Found: C, 65.5; H, 11.3; N, 11.1; molecular weight 249.

Isolation and identification of Products from 2,2,4-trimethyl-2-pentylamine. Distillation of the crude reaction mixture (see Table II) in the 20-cm. helices-packed column permitted the removal of acetone (identified as crude 2,4-dinitrophenylhydrazone, m.p. 122–122.5°; not depressed on mixing with authentic acetone 2,4-dinitrophenylhydrazone), *tert*-butyl alcohol (analyzed by functional group[28] methods and identified by infrared spectrum), water, and a large fraction of recovered amine. The last 1.5 g. of amine taken overhead at 47–65°/12–13 mm., $n_D^{20.5}$ 1.4281, was shown by infrared analysis to contain traces of *tert*-nitrooctane plus an unidentified carbonyl impurity. After removal of the unchanged amine (some was lost to *solid* carbonate formation during the reaction period, a total of 7.9 g. of reaction product remained. Further distillation gave fraction 8 (b.p. 52–53°/7 mm., $n_D^{20.5}$ 1.4335, 1.1 g.) and fraction 9 (b.p. 53–65°/7 mm., 2.9 g., empirical formula $C_{8.0}H_{22}N_{0.87}O_{1.5}$). Fractions 8 and 9 were both analyzed by infrared spectroscopy (carbon tetrachloride solution) and the spectra compared with an authentic spectrum of *tert*-nitrooctane supplied by Professor Kornblum of Purdue University. The most characteristic bands are those at 6.46–6.50 (doublet), 7.41 and 11.76 μ—all are strong bands. The %w of *tert*-nitrooctane was estimated as (utilizing the first two bands) 78 ± 5%w in fraction 8 and 78 ± 3%w in fraction 9; carbonyl impurities were present. (Lit.[8] values for *tert*-nitrooctane: b.p. 85°/20 mm.; n_D^{20} 1.4350). During the distillation a white solid crystallized from fraction 9. After recrystallization from petroleum ether (b.p. 30–60°), this solid melted at 153.5–155° (sealed tube).

Anal. Found: C, 67.2; H, 13.5; N, 12.9 (empirical formula $C_{13.9}H_{34}N_{1.1}O_{2.0}$).

Infrared analysis showed a weak band at 6.10 and a strong broad band at 6.40 μ (nitro compound?). Further identification work was not done.

There was also obtained ~1.0 g. of column holdup and 2.4 g. of kettle residue (not volatile at 140°/2 mm.) having an empirical formula $C_{7.7}H_{16}N_{1.0}O_{1.0}$. The infrared spectrum of the kettle residue showed a strong broad carbonyl band at 5.92 μ, moderately strong absorption at 6.4–6.6 μ, and a weak to moderate band at 2.97 (shoulder at 3.13 μ). It is probable that ketone condensates and some *N*-monosubstituted amides were present.

Isolation and identification of products from diisopropyl amine. Fractionation of the crude reaction mixture in the Piros-Glover column gave the following fractions:

Fraction 1 (b.p. 49–54°, n_D^{20} 1.3990, 1.7 g.) and fraction 2 (b.p. 54–56°, n_D^{20} 1.3890, 5.3 g.) were combined. An aliquot (1.338 g.) gave 1.834 g. of crude 2,4-dinitrophenylhydrazone; mixed melting point with authentic acetone 2,4-dinitrophenylhydrazone (m.p. 125–126°) showed no significant depression, 124.5–126°. Chromatographic analysis further indicated that there was essentially only one component in the crude 2,4-dinitrophenylhydrazone. Another aliquot (~0.5 ml.) was converted to the *N*-phenylthiourea in good yield; recrystallized from petroleum ether (b.p. 30–60°), m.p. 100–101° (lit. value for *N*-phenyl-*N*-isopropyl thiourea: m.p. 101°).

Anal. Calcd. for $C_{10}H_{14}N_2S$: C, 61.8; H, 7.25; N, 14.4. Found: C, 62.3; H, 7.5; N, 14.6.

---

(26) D. G. Norton, V. E. Haury, F. C. David, L. J. Mitchell, and S. A. Ballard, *J. Org. Chem.*, 19, 1054 (1954).

(27) *Anal.* Calcd. for *N*-(4-methyl-2-pentyl)acetamide ($C_8H_{17}NO$): C, 67.1; H, 12.0; N, 9.77. Calcd. for the aldol condensate of I ($C_{18}H_{35}N$): C, 81.5; H, 13.3; N, 5.27.

(28) The variation in the yields of *tert*-butyl alcohol reported in Table II results because hydroxyl values obtained by BF_3 esterification and conversion to nitrite ester were not in agreement. The reason for this discrepancy is not known.

After standing at room temperature for about 2 days, the refractive indices (n_D^{19}) of 1 and 2 were respectively 1.4043 and 1.4002.

Fractions 3 to 5 (b.p. 56–67°, n_D^{20} 1.3771 to 1.3766, 13.8 g.) on standing (~2 days) showed a change in refractive index to n_D^{19} 1.4020. Even with fractions 6 and 7 (b.p. 67–79°, n_D^{20} 1.3912 to 1.3933, 4.4 g.), the refractive index showed a small change to n_D^{19} 1.3978 on standing. The forerun fractions (Fractions 1 to 7) showed strong bands in the infrared at 2.98, 5.83, and 6.00 μ as well as a distinct shoulder at 6.25 μ (characteristic of NH_2 deformation).

Fractions 3 to 7 were combined and 0.5 ml. of concd. hydrochloric acid was added to insure that equilibrium had been reached (no change in n_D^{20} over a 2-hr. period). Solid sodium hydroxide was then added to neutralize and dry the mixture. After further drying over potassium hydroxide, rectification gave 1.2 g. of a ketimine, b.p. 93°, n_D^{20} 1.4068 (lit.[27] values for *N*-(isopropylidene)isopropylamine, b.p. 93.5°, n_D^{20} 1.4088). The infrared spectrum was compatible with known ketimine spectrum, showing only a small amount of carbonyl as impurity. In other experiments attempts were made to dry the crude reaction mixture over solid sodium or potassium hydroxide. The best yield of ketimine isolable under these conditions was 0.03 mole/0.20 mole of *tert*-butyl hydroperoxide. However, indications were that the drying operation was not complete.

The bulk of the distillate, fractions 8 to 11 (b.p. 79–85°, n_D^{20} 1.3930 to 1.3917, 48.4 g.), was shown to consist of 67 ± 1%w diisopropylamine (0.665 equiv./100 g.) by titration. The infrared spectrum was compatible with principally this amine and *tert*-butyl alcohol. Fraction 12 (b.p. 85–102°, n_D^{20} 1.3923, 0.9 g.) was distilled through the column using *n*-octane as a "pusher"; it represents principally recovered amine. A kettle residue of ~0.6 g. (corrected for *n*-octane) was not further investigated.

Isolation and identification of products from tri-n-propylamine. After removal of ether (fraction 1) used in transfer operation, Piros-Glover fractionation gave the following results.

Fractions 2 and 3 (b.p. 72–82°, 90% over at 79.5–82°, $n_D^{20.5}$ 1.3830–1.3863, 14.6 g.) were combined and shown by infrared and functional group analyses to contain *tert*-butyl alcohol (hydroxyl value 1.07 equiv./100 g.) contaminated by water (7.7%w) and a trace of carbonyl. The latter was shown to be propionaldehyde (m.p. of 2,4-dinitrophenylhydrazone 145.5–147°, not depressed by mixing with the authentic derivative).

Fraction 4 (b.p. 82–102°, $n_D^{20.5}$ 1.3879, 1.1 g.) was shown by titration to contain 3.7%w as di-*n*-propylamine and balance was ascribed to *tert*-butyl alcohol. Fractions 5 and 6 (b.p. 102–105°, 53.5–69°/200 mm., $n_D^{20.5}$ 1.4073 to 1.4091, 2.3 g.) were shown by titration to contain ~82%w di-*n*-propylamine. The infrared spectrum was compatible with this plus *tert*-butyl alcohol and water impurities. Fractions 7 and 8 (b.p. 69°/200 mm., n_D^{20} 1.4052, 4.8 g.) were titrated for amine (0.94 equiv./100 g., theory for di-*n*-propylamine is 0.99 equiv./100 g.; lit.[29] values, b.p. 110°, n_D^{20} 1.4046).

Anal. Calcd. for $C_6H_{15}N$: C, 71.3; H, 14.8; N, 13.8. Found: C, 70.5; H, 15.0; N, 13.3.

In another run this amine was converted to an *N*-phenylthiourea, m.p. 60.5–61.5°.

Anal. Calcd. for $C_{13}H_{20}N_2S$: C, 66.0; H, 8.51; N, 11.9. Found: C, 65.9; H, 8.4; N, 11.7.

This derivative showed no depression in melting point on mixing with an authentic sample prepared from di-*n*-propylamine (m.p. 61–61.5°). Although a literature value[30] of 69° is given for this derivative, the melting point observed was 61–61.5° after three recrystallizations of authentic material.

Fraction 9 (b.p. 69–102°/201 mm., $n_D^{20.5}$ 1.4083, 0.3 g.), a break cut, was followed by fractions 10 to 13 which represented recovered tri-*n*-propylamine (b.p. 87.5–89°/92 mm. to 55°/22 mm., $n_D^{20.5}$ 1.4161–1.4177, 61.2 g. or 0.43 mole).

Successively higher boiling fractions were collected as follows: fraction 14 (b.p. ≤82°–91.5°/22 mm., $n_D^{20.5}$ 1.4429, 0.5 g.), fraction 15 (b.p. 91.5°/22 mm. to 95°/5.5 mm., $n_D^{20.5}$ 1.4585, 1.2 g.), fraction 16 (b.p. 95–116°/5.5 mm., $n_D^{20.5}$ 1.4777, 1.4 g.), and a residue of 4.1 g. Fractions 14 to 16 were combined and dissolved in an ether-petroleum ether (b.p. 30–60°) mixture and extracted with 5% hydrochloric acid; the amine was liberated with base, 0.7 g., n_D^{20} 1.4618 (6.20% basic nitrogen). Infrared analyses showed the presence of carbonyl and α,β-unsaturated carbonyl impurities but the spectrum was otherwise consistent with that expected for a tertiary amine structure. Infrared analysis of the residue from the distillation also showed some carbonyl impurities, but the spectrum was compatible with principally tertiary amine (Found: 4.71 Basic N, 5.52% total N). The high boiling products from this distillation were not investigated further.

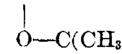
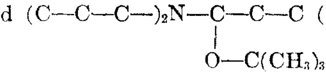
As direct distillation did not permit a satisfactory resolution of the high boiling nitrogenous products, an attempt was made to do this by preliminary separation into basic and non-basic fractions using extractive techniques. A summary of this experiment is shown in Table VII.

TABLE VII

FUNCTIONAL GROUP ANALYSIS OF THE BASIC AND NONBASIC FRACTIONS FROM TRI-*n*-PROPYLAMINE AND *tert*-BUTYL HYDROPEROXIDE[a]

Basic Fraction[c]		Nonbasic Fraction[c]	
Analysis or Product	Equivs.	Analysis	Moles
Total basic N	0.725	Total carbonyl	0.054
Sec. + tertiary amine	0.69	Total acid	0.046[d]
Tertiary amine[e]	0.52	Gases	0.0033[f]
Sec. amine (by diff.)	0.17	—	—
Di-*n*-propylamine (isolated)	0.14	—	—
Unidentified	5.6 g.[g]	—	—

[a] Bath temperature, 70° ± 3°[b]; kettle temperature, 82–68°; amounts, 0.40 mole RO_2H, 0.82 mole RNH_2; total reaction time, 8 hr.; % peroxide decomposed, 95%. [b] The bath temperature was raised to 79.5° during the last two hours of the experiment. [c] See analytical methods described previously. [d] Isolated *p*-bromophenyl propionate, but the presence of other acid (*e.g.*, 2-methyl-2-pentenoic) is probable. [e] Recovered tri-*n*-propylamine = 0.484 equiv. [f] Mass spectrometry showed principally oxygen, traces of methane, carbon dioxide, ethane, etc. There was no indication of any significant amount of C_3 fragment (propylene or propane, <0.1%). [g] See body of paper for observation on part of this material.

Distillation of the basic fraction permitted the isolation of two fractions of narrow boiling range which are referred to in the text of this paper. These fractions (respectively, $C_{9.85}H_{20.0}N_{1.00}O_{1.04}$, b.p. 98–99°/3 mm., 0.6 g.; $C_{12.8}H_{25.7}N_{1.00}O_{1.09}$, b.p. 105–107°/2 mm., 0.7 g.) were examined by infrared analysis. The spectra and elemental analyses suggested assignment of the structures  $\mathrm{C{-}C{-}C{-}NH{-}\underset{O{-}C(CH_3)_3}{\underset{|}{C}}{-}C{-}C}$ (A) and  $\mathrm{(C{-}C{-}C{-})_2N{-}\underset{O{-}C(CH_3)_3}{\underset{|}{C}}{-}C{-}C}$ (B), respectively, to the

---

(29) *Dictionary of Organic Compounds*, edited by I. Heilbron and H. M. Bunbury, Oxford Univ. Press, New York, N. Y. 1953, Vol. II, p. 438.

(30) R. L. Shriner and R. C. Fuson, "*The Systematic Identification of Organic Compounds*," John Wiley and Sons, New York, N. Y., 1948, p. 234.

principal components. The principal spectral basis for the assignment of A was a "secondary NH deformation" at 6.36 μ. In neither case could a conclusive identification be made from the infrared data, although the absence of other characteristic bands is in keeping with the "amino ether" postulate.

Acknowledgment. The author is indebted to Messrs. F. F. Rust, E. A. Youngman, G. M. Coppinger and E. J. Smutny for helpful discussions and criticism of this work.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

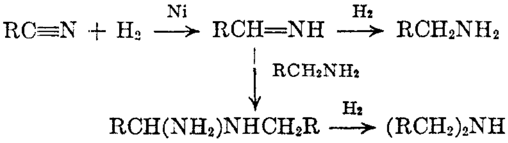
The Guerbet Reaction. I. The Reaction of Amines Under Guerbet Conditions

ROBERT E. MILLER

Received March 2, 1960

The reaction of primary amines with the structure $RCH_2CH_2NH_2$ has been studied in a Guerbet-type condensation. The principal products were the simple imines, $RCH_2CH{=}NCH_2CH_2R$, alcohols, and carbonyl compounds. With *n*-hexylamine and *n*-octylamine branched-chain trimolecular imines were also obtained. Under similar conditions nitriles were converted to amides.

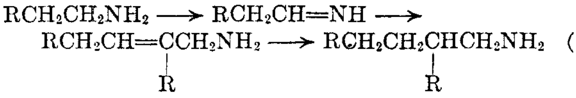
Aldimines have been postulated as the initial products in the catalytic hydrogenation of nitriles.[1] Condensation of the aldimine followed by hydrogenation results in a mixture of the simple primary amine as well as the secondary and tertiary amines derived from it.



$$\begin{array}{l} RC\equiv N + H_2 \xrightarrow{Ni} RCH{=}NH \xrightarrow{H_2} RCH_2NH_2 \\ \qquad\qquad\qquad\quad \downarrow RCH_2NH_2 \\ \qquad RCH(NH_2)NHCH_2R \xrightarrow{H_2} (RCH_2)_2NH + NH_3 \end{array}$$

(1)

It was of interest to study the behavior of amines of the structure $RCH_2CH_2NH_2$ in a Guerbet condensation. By analogy with the Guerbet reaction of alcohols,[2] the proposed reaction assumed the formation of an aldimine or ketimine intermediate, which might then attack the β-methylene group of a second molecule of the amine. This sequence would provide a synthesis for dimeric, branched-chain, primary amines.



$$\begin{array}{l} RCH_2CH_2NH_2 \longrightarrow RCH_2CH{=}NH \longrightarrow \\ \quad RCH_2CH{=}\underset{\displaystyle R}{\underset{|}{C}}CH_2NH_2 \longrightarrow RCH_2CH_2\underset{\displaystyle R}{\underset{|}{C}}HCH_2NH_2 \end{array}$$

(2)

Such products, however, were not isolated from this condensation. The principal reaction involved the formation of the simple imines, $RCH_2CH{=}N(CH_2)_2R$, derived from an aldol reaction of the aldimine or ketimine intermediate with the amine reactant. Subsequent condensation of a second molecule of the aldimine or ketimine with the Schiff base, or dimerization of the Schiff base followed by the loss of a molecule of primary amine,[3] resulted in the formation of branched-chain trimolecular imines. *N*-(2-*n*-Butyloctylidine)-*n*-hexylamine and *N*-(2-*n*-hexyl-2-decenylidene)-octylamine were isolated from the self-condensation of *n*-hexylamine and *n*-octylamine, respectively. The substitution reaction appears to take place solely at the β-methylene group of the alkylidene substituent rather than at a carbon atom of the imino moiety.

The formation of secondary amines, $(RCH_2CH_2)_2NH$, was only a minor reaction. Tertiary amines were not isolated. These results may be ascribed to the insufficiency of hydrogen present during the condensation. The amount of hydrogen liberated during the reaction is primarily limited to the dehydrogenation of the amine reactant. Of possible significance to the mechanism of the Guerbet condensation is the fact that hydrogen liberated during this dehydrogenation reaction was consumed in the saturation of the carbon-nitrogen double bond.

Identification of the imines was established by spectral analysis and subsequent conversion to a mixture of an amine and a carbonyl compound by acid hydrolysis.

Alcohols and/or carbonyl compounds derived from the starting material were also isolated. Since no attempt was made to provide anhydrous tripotassium phosphate, or to exclude air from the system, these products result from hydrolysis and/or oxidation of the aldimine or ketimine by the hot alkaline solution. This reaction is similar to the oxidation of the carbonyl intermediate in Guer-

---

(1a) H. Adkins and H. I. Cramer, *J. Am. Chem. Soc.*, **52**, 4349 (1930). (b) C. F. Winans and H. Adkins, *J. Am. Chem. Soc.*, **54**, 306 (1932). (c) W. Carothers and R. Adams, *J. Am. Chem. Soc.*, **47**, 3051 (1925). (d) B. S. Biggs and W. S. Bishop, *Ind. Eng. Chem.*, **38**, 1084 (1946). (e) J. v. Braun, G. Blessing, and F. Zobel, *Ber.*, **56**, 1988 (1932).

(2) E. F. Pratt and D. G. Kubler, *J. Am. Chem. Soc.*, **76**, 52 (1954).

(3) W. S. Emerson, S. M. Hess, and F. C. Uhle, *J. Am. Chem. Soc.*, **63**, 872 (1941).