When 160 mg (0.5 mmole) of 5-amino-4-benzylmercapto-2-*p*-nitrophenyloxazole was hydrolyzed with 31 mg (0.5 mmole) of potassium hydroxide in ethanol at 25° for 12 hr, there was obtained 24 mg (14%) of silky, white needles, mp 172–173°, identical with the product of acid hydrolysis.

4-Benzylmercapto-5-diacetylamino-2-*p*-nitrophenyloxazole.—Compound IXa (1.09 g, 3.3 mmoles), in 15 ml of acetic anhydride, and 3 ml of acetic acid was heated on a steam bath for 20 hr. After addition of 20 ml of ethanol the volume was reduced to about 5 ml which gave yellow needles, mp 118–121°. Crystallization from acetone–hexane gave 0.863 g (62%) of pale yellow needles: mp 122–123.5°; ν 1720 and 1745 cm^{-1} (Ac_2N); an AB quartet at $\delta = 8.21$ ($J = 10$ cps, *p*-nitrophenyl), a singlet at 7.24 (benzyl aromatic), a singlet at 4.23 (CH_2), and a singlet integrating for six protons at 2.15 ppm (CH_3). *Anal.* Calcd for $C_{20}H_{17}N_3O_5S$: C, 58.57; H, 4.14; N, 10.16; S, 7.77. Found: C, 58.65; H, 4.11; N, 10.20; S, 7.57.

5-Acetylamino-4-benzylmercapto-2-*p*-nitrophenyloxazole.—When IXa (0.545 g, 1.7 mmoles) was treated with 10 ml of pyridine and 10 ml of acetic anhydride for 20 hr at 25° work-up afforded a viscous, brown oil. Chromatography on acid-washed alumina (pH 6), afforded 206 mg (29%) of diacetyl compound, mp 121–123°, and 188 mg (31%) of the monoacetyl compound, mp 181–186°, which gave ν 3270 (free NH), 3185 (bonded NH), and 1675 cm^{-1} (amide C=O). *Anal.* Calcd for $C_{18}H_{15}N_3O_4S$: C, 58.52; H, 4.09; N, 11.38; S, 8.68. Found: C, 58.39; H, 4.09; N, 11.61; S, 8.74.

Refluxing the diacetyl derivative (103 mg, 0.25 mmole) for 30 min in 5 ml of ethanol containing 2 drops of 1 *N* hydrochloric acid gave 78 mg (85%) of the monoacetyl derivative, mp 185–186°, after crystallization from ethanol–water.

5-Amino-4-methylmercapto-2-*p*-nitrophenyloxazole (IXb).—S,S′-Dimethyl dithiooxaldiimidate (1 g, 6.7 mmoles) and 2.1 g (14 mmoles) of *p*-nitrobenzaldehyde were heated for 45 min on a steam bath in 2 ml of benzene containing 1 drop of glacial acetic acid. The product was collected and washed with benzene to give red crystals, 1.3 g (76%), mp 164–169°. Further crystallization from benzene gave deep red crystals, mp 170–172°. *Anal.* Calcd for $C_{10}H_9N_3O_3S$: C, 47.81; H, 3.61; N, 16.73; S, 12.76. Found: C, 47.63; H, 3.42; N, 16.82; S, 12.92.

5-*p*-Nitrobenzylideneamino-4-phenylmercapto-2-*p*-nitrophenyloxazole (Ve).—S,S′-Diphenyl dithiooxaldiimidate (1.36 g, 5 mmoles), 1.66 g (11 mmoles) of *p*-nitrobenzaldehyde, and 2 ml of acetone were heated on a steam bath for 16 hr. After cooling, the crystalline product was separated and washed with acetone to give 1.35 g of dull, orange crystals. Recrystallization from acetone afforded 1.02 g (70%), mp 198–198.5°, of bright orange crystals. *Anal.* Calcd for $C_{22}H_{14}N_4O_6S$: C, 59.20; H, 3.16; N, 12.55; S, 7.18. Found: C, 58.99; H, 3.17; N, 12.64; S, 7.10.

Attempted Acylations of Va.—Compound Va (1 g, 3.3 mmoles) was refluxed for 2 hr in 10 ml of acetic anhydride and 3 ml of acetic acid. Addition of 20 ml of absolute ethanol, removal of volatile material, and dilution with 5 ml of absolute ethanol, gave yellow needles of Va, mp 100–103°. Addition of water to the mother liquor gave white crystals of α-benzoylamino-α-methylmercaptoacetonitrile (VI), mp 130–134°.

A similar experiment with refluxing acetic anhydride (10 ml) and pyridine (10 ml) gave only starting material after dilution with ethanol and evaporation of volatile material.

Compound Va (294 mg, 1 mmole), 0.4 g (3 mmoles) of benzoyl chloride, and 10 ml of pyridine were heated on a steam bath for 30 min. Neutralization with sodium bicarbonate at 5° gave, after crystallization from ethanol, 250 mg of the starting material Va. Repetition of the reaction for 12 hr under reflux also afforded only starting material.

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The Reaction of Diisopropyl Peroxydicarbonate with N,N-Dimethylaniline and N-Methyldiphenylamine

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Diisopropyl peroxydicarbonate (IPP) and N,N-dimethylaniline react at 8° in benzene to form carbon dioxide, isopropyl alcohol, and N-isopropoxymethyl-N-methylaniline as the major products. Carbon dioxide and isopropyl alcohol are also formed along with N-isopropoxymethyldiphenylamine in the reaction of IPP and N-methyldiphenylamine at 20°. A free-radical chain mechanism involving intermediate aminomethyl radicals is proposed for these reactions.

The reaction of diacyl peroxides, especially benzoyl peroxide, with N,N-dimethylaniline (DMA) has been studied rather extensively.[1-7] The present investigation was undertaken to study the reaction of diisopropyl peroxydicarbonate[8,9] (IPP) with tertiary amines. The initial studies have been carried out with DMA and N-methyldiphenylamine.

The reaction of IPP with DMA in benzene at 8° was much too rapid at reasonable concentrations for an accurate study of the kinetics by iodometric titration. For example, starting with initial concentrations of IPP and DMA of 0.0256 and 0.125 *M*, respectively, the half-life of the reaction was less than 30 sec. Significantly, running the reaction in a solvent containing 90 vol % benzene and 10% styrene led to an increase in the half-life by a factor of about 10.

The reaction of IPP with MDPA in benzene was much slower than that with DMA. It was studied at 10.0, 20.0, and 30.0° in all cases using a large excess of amine. Good pseudo-first-order rate plots were obtained during at least 1.5 half-lives in each case. The reaction is also first order in amine. Therefore, the kinetic expression describing the rate of reaction is as follows.

$$\text{rate} = k_2[\text{IPP}][\text{MDPA}]$$

(1) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 590–594.

(2) (a) L. Horner and E. Schwenk, *Angew. Chem.*, **61**, 411 (1949); *Ann.*, **566**, 69 (1950); (b) L. Horner and K. Scherf, *ibid.*, **573**, 35 (1951); (c) L. Horner and C. Betzel, *ibid.*, **579**, 175 (1953); (d) L. Horner and H. Junkermann, *ibid.*, **591**, 53 (1955); (e) L. Horner, *J. Polymer Sci.*, **18**, 438 (1955); (f) L. Horner and B. Anders, *Chem. Ber.*, **95**, 2470 (1962).

(3) (a) M. Imoto, T. Otsu, and K. Kimura, *J. Polymer Sci.*, **15**, 475 (1955); (b) M. Imoto and S. Choe, *ibid.*, **15**, 485 (1955); (c) M. Imoto, T. Otsu, and T. Ota, *Makromol. Chem.*, **16**, 10 (1955); (d) M. Imoto, S. Choe, and H. Taketsugi, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **58**, 451 (1955); (e) M. Imoto and K. Takemoto, *J. Polymer Sci.*, **19**, 579 (1956).

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(7) D. M. Graham and R. B. Mesrobian, *Can. J. Chem.*, **41**, 2938 (1963).

(8) F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *J. Am. Chem. Soc.*, **72**, 1254 (1950).

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A summary of the kinetic data is given in Table I.

It can be seen from the information presented in Table II that the reaction is retarded by styrene or 2,2′-methylenebis(4-methyl-6-*t*-butyl)phenol.

TABLE I

RATE CONSTANTS FOR IPP–MDPA REACTION[a]

Temp, °C	[MDPA], *M*	$k_1 \times 10^4$ sec^{-1}	k_2[b] $\times 10^4$ mole^{-1} sec^{-1}
10.0	0.266	1.77 ± 0.02[c]	6.65 ± 0.08[c]
20.0	0.266	5.35 ± 0.48	20.1 ± 1.8
	0.399	8.02 ± 0.33	20.1 ± 0.82
30.0	0.266	17.0 ± 0.5	63.9 + 2
20.0	0.00	0.05	

[a] Initial concentration of IPP = 0.027 mole/l. [b] The Arrhenius equation constants from this data are $E^* = 19.4 \pm 0.9$ kcal/mole; $\log A = 11.8 \pm 0.7$. [c] Average deviation of at least three determinations.

TABLE II

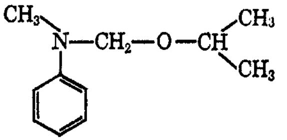
RATE CONSTANTS FOR IPP–MDPA REACTION AT 20°[a]

Additive	Additive, mole/l.	$k_2 \times 10^4$ mole^{-1} sec^{-1}
None	...	20.1
Styrene	0.87	5.74
2,2′-Methylenebis(4-methyl-6-*t*-butyl)phenol	0.00158	6.80

[a] Initial concentrations of IPP and MDPA = 0.027 and 0.266 mole/l., respectively.

In both the IPP–DMA and IPP–MDPA reactions, the only volatile products detected were carbon dioxide and isopropyl alcohol. No evidence for acetaldehyde or acetone was found.

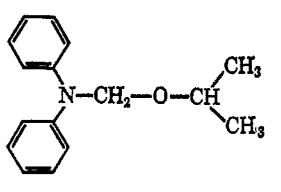
In the IPP–DMA reaction another product could be isolated (in 93 mole % purity) by reduced pressure distillation. This colorless, liquid product was identified as N-isopropoxymethyl-N-methylaniline (I) from its elemental analyses, infrared spectrum, and mainly through its nmr spectrum.



I

The integrated nmr spectrum of I (in $CDCl_3$) was unequivocal. The presence of the isopropoxy group was shown by the six-proton doublet at τ 8.83 plus the symmetrical multiplet (one proton) at 6.32. The N-methyl absorption appeared at τ 6.97 (three protons). This was a slight shift from the DMA methyl proton singlet at τ 7.18. A two-proton absorption singlet appeared at τ 5.23, which can be assigned to the NCH_2O protons.

The product corresponding to I in the MDPA–IPP reaction would be N-isopropoxymethyldiphenylamine (II).



II

Although II was not isolated, its presence as the major nonvolatile product was indicated by the infrared and nmr spectra of the residue remaining after the removal of the volatile products. This mixture was shown by thin layer chromatography to contain mainly MDPA plus one major product. The infrared spectrum of the mixture was similar to that of MDPA except for a weak band at 1000 cm^{-1} which can be assigned to the ether linkage. The nmr spectrum of the residue was equivalent to the spectrum of MDPA plus a doublet at τ 8.94 [$CH(CH_3)_2$], a multiplet at 6.15 [$CH(CH_3)_2$], and a singlet at 4.90 (NCH_2O) all of low intensity.

The yields of the various products in the IPP–amine reactions are given in Table III.

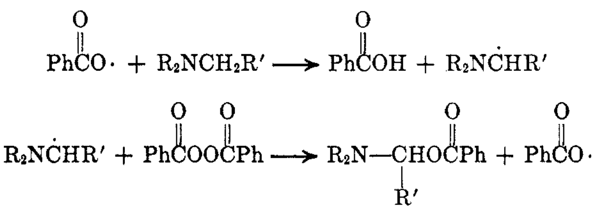
TABLE III

YIELDS OF PRODUCTS IN IPP–AMINE REACTIONS (MOLES OF PRODUCT PER MOLE OF IPP DECOMPOSED)

Reaction	IPP–DMA at 8°	IPP–MDPA at 20°
Carbon dioxide	2.0	1.9
Isopropyl alcohol	1.1	1.1
$R_2NCH_2OCH(CH_3)_2$	0.5[a] (0.8)[b]	0.75[c]

[a] Isolated. [b] Approximated by isolation plus tlc and weight of residue. [c] Calculated from nmr spectrum.

Any decision as to the mechanism of the IPP–DMA or IPP–MDPA reaction would be obviously premature. However, it does appear that the kinetics of the IPP–MDPA reaction are best explained by the presence of a free-radical chain similar to that proposed by Hrabak and Vacek for the benzoyl peroxide–tertiary amine reaction[6]. According to their scheme, the kinetic chain is initiated by a bimolecular reaction of amine and peroxide which produces benzoyloxy radicals. This is followed by two chain-propagation reactions involving hydrogen abstraction from the tertiary amine and radical displacement on the peroxide linkage by the resulting α-amino-radical.



$$\mathrm{Ph\overset{\overset{O}{\|}}{C}O\cdot + R_2NCH_2R' \longrightarrow Ph\overset{\overset{O}{\|}}{C}OH + R_2N\dot{C}HR'}$$

$$\mathrm{R_2N\dot{C}HR' + Ph\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}Ph \longrightarrow R_2N{-}\underset{\underset{R'}{|}}{C}HO\overset{\overset{O}{\|}}{C}Ph + Ph\overset{\overset{O}{\|}}{C}O\cdot}$$

In the case of the IPP–MDPA reaction, the fact that the addition of styrene or 2,2′-methylene-bis(4-methyl-6-*t*-butyl)phenol resulted in a moderate retardation of the reaction indicates either the existence of a short kinetic chain or the coexistence of the radical-chain mechanism with a nonchain process.[2f]

By analogy to the mechanisms proposed by Hrabek and Vacek[6] for the chain reaction and by Horner and Anders[2f] for the possibly concurrent nonchain process, the expected product of the IPP–DMA or IPP–MDPA reaction would be an α-aminomethyl isopropyl carbonate. Instead, the product actually obtained is an α-aminomethyl isopropyl ether. More information is needed to allow an explanation for this apparent anomaly. Possibly, the carbonate is formed and then loses carbon dioxide. The loss of carbon dioxide could take place intramolecularly or by a displacement reaction with isopropyl alcohol.

Experimental Section

1. **Materials.**—The diisopropyl peroxydicarbonate[9] used was the commercial grade produced by Pittsburgh Plate Glass, Chemical Division. The active oxygen assay was always greater than 99% of the theoretical. The N,N-dimethylaniline (Matheson Coleman and Bell; free from mono-) and N-methyldiphenylamine (Eastman Organic Chemicals) were purified by vacuum distillation through a 12-in. packed column. They were stored in sealed vials. Benzene (Baker Analyzed Reagent, thiophene free) was distilled under nitrogen through a 24-in. Vigreux column. The benzene was placed in a bottle sealed with a serum cap and completely stripped of oxygen by alternately freezing, evacuating, thawing, and adding nitrogen several times. Styrene (Matheson Coleman and Bell) was distilled under 15 mm of nitrogen through a 24-in. Vigreux column. 2,2′-Methylenebis(4-methyl-6-*t*-butyl)phenol (American Cyanamide 2246 antioxidant) was used without purification. Airco prepurified nitrogen was used. Matheson "bone dry" carbon dioxide was used.

2. **Kinetics.**—The reactions were carried out in 50-ml flasks equipped with a serum caps and a mercury seals. The flask was stripped of oxygen by several alternate evacuations and additions of nitrogen. The solvent was equilibrated at the temperature of the run and then 20.0 ml was injected into the reaction flask. Styrene, when used, was treated similarly.

The amine was allowed to equilibrate at 20°, measured out to the nearest 0.002 ml using a 2-ml micrometer syringe, and injected into the flask. The flask and contents were thermostated at the temperature of the run and then liquid IPP at its melting point (8–10°) was measured out to the nearest 0.01 ml in a syringe and quickly injected into the reaction mixture. The mixture was shaken and a 1.00-ml aliquot was taken immediately with a 1-ml syringe. This aliquot was placed in a 50-ml flask containing 10 ml of acetone, 1 ml of 20% aqueous potassium iodide, and 1 ml of 10% aqueous acetic acid. The iodine liberated was titrated to a colorless end point with 0.0200 *N* thiosulfate solution.

The time of this first aliquot was taken as the zero time. One-milliliter aliquots were then taken periodically and treated identically.

When 2,2′-methylenebis(4-methyl-6-*t*-butyl)phenol was used, it was placed in the flask prior to oxygen stripping.

3. **Products.**—In the IPP–DMA reaction, the products were determined using the following procedure.

(a) The mercury seal used during the kinetic studies was replaced with a Dry Ice trap followed by two 150-mm drying tubes, both filled with Ascarite and anhydrous magnesium perchlorate.

(b) After the reaction was complete the volatile material in the reaction flask was transferred to the Dry Ice trap with a stream of nitrogen, the contents of the flask being kept at 8°. In this process, the carbon dioxide was quantitatively captured in the first Ascarite trap. The solvent and volatile products (*e.g.*, isopropyl alcohol) were condensed in the Dry Ice trap, and the DMA and other nonvolatile residues remained in the flask.

(c) The amount of carbon dioxide evolved was determined from the weight gain of the Ascarite trap. The qualitative and quantitative analyses of the materials in the Dry Ice trap were carried out by gas chromatography using a 2-m Ucon Polar colum at 50°.

(d) The DMA remaining in the reaction flask was isolated by vacuum distillation by equipping the flask with a 6-in. Vigreux column and evacuating at 25° (0.01–0.03 mm) trapping the DMA in Dry Ice.

(e) Another compound was isolable by distillation from the residue of the DMA distillation. This material boiled at 30–35° (0.02–0.03 mm). Using this procedure a sample of this unknown could be obtained which was 93 mole % pure (analysis by nmr).[10]

Anal. Calcd for $C_{11}H_{17}NO$ (contained 7 mole % $C_8H_{11}N$): C, 73.98; H, 9.54; N, 8.01; O, 8.47. Found: C, 73.5; H, 9.62; N, 8.58; O, 8.64.

The infrared spectrum (neat) showed bands at 3012 (w), 2961 (s), 2910 (m), 2880 (m), 1591 (s), 1492 (s), 1356 (m), 1330 (m), 1260 (w), 1217 (m), 1110 (m), 1005 (s), 991 (w), 949 (w), 749 (s), and 680 cm^{-1} (m). This spectrum is almost identical with that of DMA, the major exceptions being in the following regions: 2800–3000, 1320–1360, and 1005 cm^{-1}.

The nmr spectrum in $CDCl_3$ (corrected for DMA impurity) showed a doublet at τ 8.83 (J = 6 cps, six protons), a singlet at 6.97 (three protons), a symmetrical multiplet at 6.32 (J = 6 cps, one proton), a singlet at 5.23 (two protons), and a complex multiplet at 2.7–3.3 (five protons). The DMA methyl proton singlet appears at τ 7.18.

(f) Thin layer chromatography of the residue after distillation (silica gel, developed with benzene, visualization with iodine vapor, oxygen-free atmosphere during development) always indicated a mixture containing mostly the unknown discussed above. There are at least two other minor products. The only differences between the infrared spectrum of the residue and that of the distilled unknown were a slight decrease in the absorption band at 2961 cm^{-1} and the appearance of weak bands at 1761, 1250, and 792 cm^{-1}.

In the IPP–MDPA reaction (1:10 mole ratio), the volatile products were analyzed by repeating steps a, b, and c given above. A thin layer chromatogram of the residue after the solvent and volatiles had been blown off with nitrogen indicate one major product. The infrared spectrum of this residue (neat) was identical with that of MDPA except for a weak band at 1000 cm^{-1}. An nmr spectrum (CCl_4) showed the MDPA methyl proton singlet at τ 6.76 and the MDPA phenyl proton multiplet at 2.3–3.1 plus a low-intensity doublet at 8.94 ($J \sim 7$ cps), a very low-intensity multiplet at 6.15, and a low-intensity singlet at 4.90. The ratio of the area under the MDPA methyl proton singlet to that under the doublet τ (8.94) is approximately 8.5:1. The areas under this doublet and the τ 4.90 singlet have a ratio of 3:1.

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[10] Attempts at further purification using gas chromatography were unsuccessful owing to the apparent thermal instability of this product.