residues on treatment with aqueous solutions of S-benzylthiouronium chloride gave crude salts, which were crystallized from water and dried. The m.p.'s were: pure authentic S-benzylthiuronium β-(4-iodophenoxy)-ethanesulfonate (X), 155–156°; salt from VI, 153–156°; mixed m.p. of X with salt from VI, 153–156°; salt from IX, 153–155°; mixed m.p. of X with salt from IX, 153–156°.

4-(Carboxymethoxy)-diphenyliodonium Iodide (XI).—To a stirred solution of 7.2 g. (22.4 mmoles) of phenyliodoso diacetate in 20 ml. of acetic anhydride held at or below 0° there were added first 1.2 ml. (22.4 mmoles) of concentrated sulfuric acid and then a suspension of 3.4 g. (22.4 mmoles) of phenoxyacetic acid in 30 ml. of acetic anhydride. The solution was allowed to warm to room temperature and was stirred overnight.

After solvent had been removed *in vacuo* below 70°, the residue was dissolved in 40 ml. of water, extracted three times with ether and treated with aqueous potassium iodide (3.7 g., 22.4 mmoles). The solution stood for several hours at 0° giving a colorless precipitate of **4-(carboxymethoxy)-diphenyliodonium iodide (XI)**, which after drying weighed 9.15 g. (19 mmoles, 85%). Recrystallization from water gave a constant m.p. of 108–111° (introduced onto Kofler hot-stage at 95°).

Anal. Calcd. for $C_{14}H_{12}I_2O_3$: C, 34.88; H, 2.51. Found: C, 34.79; H, 2.27.

4-(Carboxymethoxy)-diphenyliodonium Betaine (XIa).—A sample of the above acid XI (1.8 g., 3.7 mmoles) was dissolved in hot water and titrated with 0.1 *N* sodium hydroxide to a brom phenol blue end-point (*p*H 6.0–7.6). (Potentiometric titration had shown the end-point to be near *p*H 6.5.) Dilution of the solution with acetone precipitated the betaine XIa as a colorless powder. Recrystallization could be accomplished by solution in hot water and addition of acetone to incipient turbidity, followed by keeping near 0° for several hours. After drying for three hours at 100°, such material had a m.p. of 205–207° (introduced onto Kofler hot-stage at 190°).

Anal. Calcd. for $C_{14}H_{11}IO_3$: C, 47.48; H, 3.13. Found: C, 47.20; H, 3.32.

4,4'-Bis-(carboxymethoxy)-diphenyliodonium Betaine (XIIa).—After 1.4 ml. (25 mmoles) of concentrated sulfuric acid had been added to a solution of 40 mmoles of iodine(III) trifluoroacetate in 50 ml. of acetic anhydride at −20°, the solution was cooled to −40°, and 24.3 g. (160 mmoles) of phenoxyacetic acid was added in small portions and with good agitation. The solution was allowed to warm to room temperature over four hours, solvent was removed *in vacuo* below 70°, and 75 ml. of water was added. The aqueous suspension was extracted thoroughly with ether and was then filtered. The clear filtrate was made slightly alkaline with barium hydroxide, treated with carbon dioxide, filtered and passed through a Dowex-50 ion-exchange column in the acid form. The chilled eluate gave 4.0 g. (9.4 mmoles, 23%) of 4,4'-bis-(carboxymethoxy)-diphenyliodonium betaine (XIIa). Recrystallization from water–acetone and vacuum drying at 100° gave material of m.p. 212–215° (inserted onto Kofler hot-stage at 195°), unchanged by further crystallization.

Anal. Calcd. for $C_{16}H_{13}IO_6$: C, 44.88; H, 3.06. Found: C, 45.07; H, 3.27.

4,4'-Bis-(carboxymethoxy)-diphenyliodonium Iodide (XII).—Betaine XIIa (337 mg., 0.79 mmole) dissolved in 20 ml. of hot 20% hydriodic acid gave on cooling colorless needles, which were dried *in vacuo*, washed with anhydrous ether and redried, giving 354 mg. (0.64 mmole, 81%) of **4,4'-bis-(carboxymethoxy)-diphenyliodonium iodide (XII)** as a yellow powder, m.p. 162–164°.

Anal. Calcd. for $C_{16}H_{14}I_2O_6$: C, 34.55; H, 2.54. Found: C, 34.45; H, 2.83.

Attempts to crystallize XII from water gave mixtures of XII and XIIa (formed by loss of hydrogen iodide).

Structure Proofs for Salts XI and XII from Phenoxyacetic Acid.—A sample of 4-(carboxymethoxy)-diphenyliodonium iodide (XI) was heated at 120° for 2 hours. The product was crystallized twice from methylene chloride and twice from ethanol–water to give 4-iodophenoxyacetic acid of m.p. 158–160°, undepressed by admixture with an authentic sample.

Similarly, the decomposition of 4,4'-bis-(carboxymethoxy)-diphenyliodonium iodide (XII) at 165–170° gave 4-iodophenoxyacetic acid of m.p. 156–158° after two crystallizations from methylene chloride and one from ethanol-water; no depression of m.p. on admixture with an authentic sample.

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[CONTRIBUTION NO. 469 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Mechanism of the Photoöxidation of Amides

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The photoöxidation of N-alkyl amides has been studied using N-pentylhexanamide as a representative of this class. The major products formed were *n*-valeraldehyde and valeric acid from the amine part of the molecule and hexanoic acid and hexanamide from the acid part of the molecule. Formation of these products indicates that photoöxidation involves oxygen attack on the methylene group adjacent to nitrogen. This conclusion has been substantiated by examination of amides substituted with alkyl groups at various positions.

There are a number of reports in the literature on the photochemistry of amides. Examples include studies of the photodegradation of serum albumin[1] and of polyamides.[2] It has been suggested that photodegradation involves reactions of acyl and imino free radicals generated by photolytic scission of the amide group. That photolytic scission occurs under certain conditions was demonstrated by Rideal and Mitchell[3] who irradiated monolayers of stearanilide upon aqueous acid supports with light of wave length 2350–2500 Å. The photolysis products, stearic acid and aniline, appeared to have been formed by reaction of acyl and imino free radicals, respectively, with water. Later, Carpenter[4] reported that N-benzylstearamide and N-β-phenylethylstearamide were degraded in the same manner.

Since comparable studies on simple N-alkyl amides have not been reported, an investigation of the photoöxidation of a representative member of this class was undertaken. *N*-Pentylhexanamide was chosen for study principally because of its low melting point (37–38°). This amide could be examined in the liquid state at temperatures low

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[1] E. K. Rideal and R. Roberts, *Proc. Roy. Soc.* (*London*), **A205**, 391 (1951); R. Roberts, *J. Soc. Dyers and Colourists*, **65**, 699 (1949).

[2] B. G. Achhammer, F. W. Reinhart and G. M. Kline, *J. Research Natl. Bur. Standards*, **46**, 391 (1951).

[3] E. K. Rideal and J. S. Mitchell, *Proc. Roy. Soc.* (*London*), **A159**, 206 (1937).

[4] D. C. Carpenter, THIS JOURNAL, **62**, 289 (1940).

enough to avoid complicating side reactions brought about by heat. Because we were interested in reactions that would occur in sunlight, which has very little radiation below 3000 Å., exposures were made in Pyrex glass equipment using a medium pressure mercury lamp. Photoöxidation proceeded at a significant rate even though the light employed is absorbed only weakly by the amide. However, long exposures were required to obtain gross amounts of photoöxidation products.

Oxygen was absorbed during ultraviolet irradiation of N-pentylhexanamide at 50° to the extent of about 300 ml. in 285 hours. A variety of products were formed including acids, aldehydes and, surprisingly, hexanamide. Evidence for the presence of amines was not obtained. Other nitrogen-containing compounds that might be expected as a result of complicated transformations, such as ammonia, hydroxylamine and hydrazine, were also absent.

The acids formed were separated chromatographically[5,6] and identified by comparison of elution times with authentic samples and by preparation of anilide derivatives. In a typical experiment in which 10 g. of N-pentylhexanamide was exposed for 285 hours, roughly 500 mg. of mixed acids was formed. Of this amount 250 mg. was hexanoic acid and 150 mg. was valeric acid. The remainder was composed of formic, acetic and propionic acids together with a small unknown fraction.

Aldehydes were isolated as 2,4-dinitrophenylhydrazones. The latter were separated chromatographically[7] into the five fractions shown in Table I. Four of these aldehyde derivatives were identified by correspondence of their X-ray diffraction patterns to those of authentic samples. The major constituent of the mixture was the 2,4-dinitrophenylhydrazone of *n*-valeraldehyde.

TABLE I

CHROMATOGRAPHIC SEPARATION OF ALDEHYDE 2,4-DINITROPHENYLHYDRAZONES OBTAINED DURING EXPOSURE OF 10 G. OF N-PENTYLHEXANAMIDE FOR 285 HOURS

Location on column	Aldehyde	M.p., °C. of product isolated	2,4-Dinitrophenylhydrazone, mg.
Top band	Acetaldehyde	146.5–150.5	<1
Second band	Propionaldehyde	143–148	1
Third band	*n*-Butyraldehyde + an unknown	109–121	16
Fourth band	*n*-Valeraldehyde	106–109	110
Fraction washed through column	Unknown	136–141	1–2

The other major product, hexanamide, was found in the solid residue obtained by evaporation of water extracts of exposed N-pentylhexanamide. Because of purification difficulties, measurement of the amount formed was less accurate than those for the acidic and aldehyde components. However, best estimates indicated that 240 mg. (1.83×10^{-3} mole) of hexanamide was formed from 10 g. of N-pentylhexanamide during 285 hours of irradiation. This is equivalent to the combined amounts of valeraldehyde (35 mg., 0.41×10^{-3} mole) and valeric acid (143 mg., 1.40×10^{-3} mole) isolated from similar exposures.

The only gaseous products positively identified were carbon dioxide and carbon monoxide. An estimation of the rate of formation of these gases was hampered by poor reproducibility of the analyses. However, a typical analysis of the gas over the amide after 285 hours exposure as compared to initial composition of the oxygen used is given in Table II.

TABLE II

GASEOUS PRODUCTS FORMED BY ULTRAVIOLET IRRADIATION OF N-PENTYLHEXANAMIDE

	Analysis of the gas over the amide	
	Before exposure, mole %	After exposure, mole %
Carbon dioxide	Nil	1.4
Carbon monoxide	0.6	1.0
Hydrocarbons	Nil	0.3
Hydrogen	0.3	0.4
Nitrogen	0.3	3.7
Oxygen	98.8	93.2

From these data it was calculated that roughly 20 mg. of carbon dioxide and 10 mg. of carbon monoxide were formed. The assay for hydrogen is within the limits of experimental error. Nitrogen appeared in all experiments despite careful efforts to avoid contamination from the air.

The parts of the amide molecule from which these products were derived were determined unequivocally by use of carbon-14. Photoöxidation of N-pentyl-1-C^{14}-hexanamide, in which the radioactive atom is in the amine part of the molecule adjacent to nitrogen, gave radioactive valeraldehyde and valeric acid. This is illustrated in Table III.

TABLE III

DISTRIBUTION OF RADIOACTIVITY IN PRODUCTS FORMED BY PHOTOÖXIDATION OF RADIOACTIVE AMIDES

Activities are given in percentage of the maximum theoretical activity calculated assuming all of the compound came from the labeled position. These activities were measured on samples prepared by plating the compound or a derivative of it on planchets. In some cases the compounds were converted to CO_2 and counted in the form of barium carbonate.

	$C_5H_{11}CO$-$NHC^{14}H_2$ C_4H_9	$C_5H_{11}C^{14}O$-NHC_5H_{11}	$C_4H_9C^{14}H_2$-$CONHC_5H_{11}$
n-Valeraldehyde	96	Inact.	6
n-Butyraldehyde + an unknown	Inact.	Inact.	Inact.
Propionaldehyde	Inact.	Inact.	Inact.
Acetaldehyde	7	Inact.	Nil
Valeric acid	88	Inact.	7
Hexanoic acid	Inact.	85	98
Hexanamide	9	..	..
CO_2	41	18	Nil
CO	20	Inact.	Nil

The hexanoic acid isolated was completely inactive. Activity of the hexanamide was very low and was probably the result of contamination with small amounts of unchanged N-pentyl-1-C^{14}-hexanamide. N-Pentylhexanamide-1-C^{14} and N-pentylhexanamide-2-C^{14} gave radioactive hexanoic acid, but inactive valeraldehyde and valeric acid. Thus, it was established that valeraldehyde and valeric acid came from the amine part of the molecule, and

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[5] L. L. Ramsey and W. I. Patterson, *J. Assoc. Offic. Agr. Chemists*, **31**, 139 (1948).

[6] C. S. Marvel and R. D. Rands, Jr., THIS JOURNAL, **72**, 2642 (1950).

[7] J. D. Roberts and C. Green, *Ind. Eng. Chem., Anal. Ed.*, **18**, 335 (1946).

hexanoic acid and hexanamide were derived from the acyl group.

It is to be noted that significant proportions of the carbon dioxide and carbon monoxide were derived from the methylene group adjacent to nitrogen. Essentially none of these compounds arose by oxidation of the methylene adjacent to carbonyl. *n*-Butyraldehyde, propionaldehyde and acetaldehyde were inactive and thus did not include any of of the labeled positions. It is suggested that they were formed by decomposition of valeraldehyde and valeric acid.

The discovery that *n*-valeraldehyde is formed by oxidation of the amine part of the molecule and the isolation of hexanamide suggest that photooxidation involves oxygen attack at the methylene group next to nitrogen. That such is the case has been established with certainty by examination of amides substituted with methyl groups in various parts of the molecule.

The amides listed in Table IV were exposed to ultraviolet radiation in the presence of oxygen under the same conditions used for N-pentylhexanamide. These amides are previously unreported compounds. Oxygen absorption and acid formation were used as criteria of the destruction of amide by photoöxidation.

TABLE IV

PHOTOÖXIDATION OF SUBSTITUTED AMIDES

		Oxygen consumed[a]	Acid titer[b]
I	$C_4H_9CONHC(CH_3)_2C_2H_5$	0	0.15
II	$C_5H_{11}CONHC(CH_3)HC_2H_5$	23	0.25
III	$C_5H_{11}CONHCH_2C(CH_3)_2CH_3$	130	0.83
IV	$C_2H_5C(CH_3)_2CONHC_5H_{11}$	337	1.30
V	$C_5H_{11}CONHC_5H_{11}$	330	2.70
VI	$C_5H_{11}CON(CH_3)C_2H_5$	390	2.86

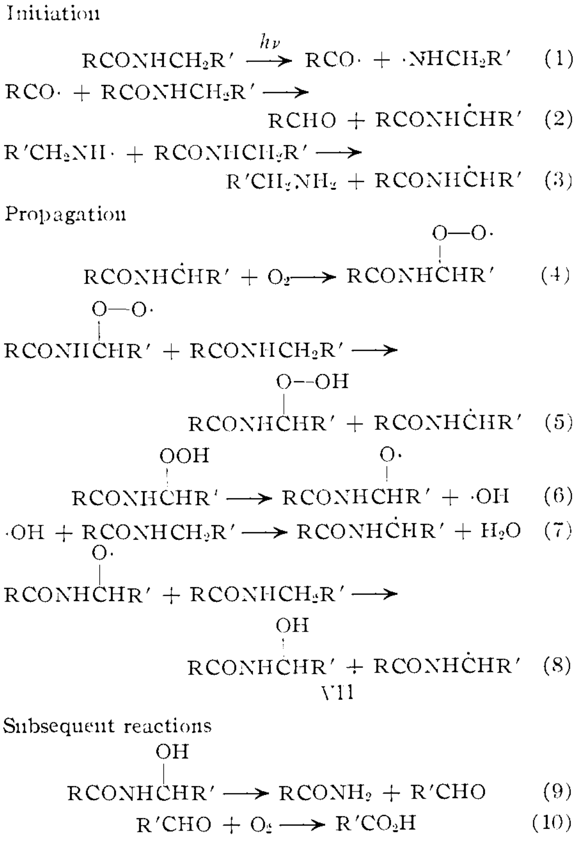
[a] Ml. of oxygen absorbed by 10 g. of amide in 285 hours at 50°. [b] Ml. 0.1 *N* NaOH per gram of exposed amide.

As shown in Table IV, N-(1,1-dimethylpropyl)-valeramide (I) did not absorb oxygen even when exposed for as long as 285 hours at 50°. Under similar conditions an amide containing one methyl group at the carbon next to nitrogen, N-(1-methylpropyl)-hexanamide (II), was also surprisingly resistant to photoöxidation although it did absorb appreciable amounts of oxygen. Substitution at the second carbon away from the amide group, illustrated by N-(2,2-dimethylpropyl)-hexanamide (III), gave much less protection. The carbon atom next to carbonyl in the acid part of the molecule is not attacked to any appreciable extent. This was shown by use of N-pentyl-2,2-dimethylbutyramide, which consumed oxygen at the same rate as a straight chain amide, N-pentylhexanamide (V). N-Methyl-N-ethylhexanamide (VI) reacted with oxygen more rapidly than the other amides examined, which indicates that amides having two alkyl groups on the nitrogen are more susceptible to photoöxidation than monoalkyl amides.

Of the products formed during photoöxidation of amides, the most easily detected are acids. Titration of the exposed amide samples (Table IV) demonstrated that amounts of acids produced during photoöxidation follow closely the pattern set by oxygen absorption. Degradation to acids of the amide completely substituted with methyl groups at the methylene next to nitrogen (I) was very low. This is in contrast to amides substituted in the acid portion (IV), the unbranched amide (V) and the dialkyl amide (VI), all of which were photoöxidized to acidic products in considerable quantities. Only small amounts of acids were formed from the amide substituted with one methyl group on the carbon next to nitrogen (II).

Another measure of amide oxidation, namely, generation of ultraviolet-absorbing materials, was investigated. All of the amides used in this study absorbed very weakly in the region 2600–3000 Å. Examination of the ultraviolet spectra of these amides after exposure, given in Fig. 1, shows the amide substituted at the carbon next to nitrogen (I) was not degraded to ultraviolet-absorbing compounds. All of the other amides formed ultraviolet-absorbing compounds. The dialkyl amide VI, which has the greatest number of hydrogen atoms next to nitrogen, showed the greatest increase in ultraviolet absorption. Only a small increase in absorption was obtained with the amide having only one hydrogen next to nitrogen (II).

These data and the discovery that photoöxidation of the unbranched amide attacks initially the amine part of the molecule lead to the conclusion that the major reaction in amide photoöxidation is oxygen attack at the methylene adjacent to nitrogen. The following mechanism is proposed to account for the breakdown of a straight chain amide.



Initiation

$$RCONHCH_2R' \xrightarrow{h\nu} RCO\cdot + \cdot NHCH_2R' \quad (1)$$

$$RCO\cdot + RCONHCH_2R' \longrightarrow RCHO + RCONH\dot{C}HR' \quad (2)$$

$$R'CH_2NH\cdot + RCONHCH_2R' \longrightarrow R'CH_2NH_2 + RCONH\dot{C}HR' \quad (3)$$

Propagation

$$RCONH\dot{C}HR' + O_2 \longrightarrow RCONH\overset{\overset{O-O\cdot}{|}}{C}HR' \quad (4)$$

$$RCONH\overset{\overset{O-O\cdot}{|}}{C}HR' + RCONHCH_2R' \longrightarrow RCONH\overset{\overset{O-OH}{|}}{C}HR' + RCONH\dot{C}HR' \quad (5)$$

$$RCONH\overset{\overset{OOH}{|}}{C}HR' \longrightarrow RCONH\overset{\overset{O\cdot}{|}}{C}HR' + \cdot OH \quad (6)$$

$$\cdot OH + RCONHCH_2R' \longrightarrow RCONH\dot{C}HR' + H_2O \quad (7)$$

$$RCONH\overset{\overset{O\cdot}{|}}{C}HR' + RCONHCH_2R' \longrightarrow \underset{\text{VII}}{RCONH\overset{\overset{OH}{|}}{C}HR'} + RCONH\dot{C}HR' \quad (8)$$

Subsequent reactions

$$RCONH\overset{\overset{OH}{|}}{C}HR' \longrightarrow RCONH_2 + R'CHO \quad (9)$$

$$R'CHO + O_2 \longrightarrow R'CO_2H \quad (10)$$

Photolytic scission of an amide bond to imino and acyl free radicals as postulated in reaction 1 has been suggested by Rideal and Mitchell.[3] No evidence for it was obtained in the present work since neither hexanaldehyde nor pentylamine was found in the photoöxidation products of N-pentylhexanamide. However, both could have been formed and oxidized to hexanoic acid and valeraldehyde, respectively, which are major photoöxidation products. Initiation by other photoactivated species, *e.g.*, a triplet state diradical of the original amide, is also possible.

The propagation reactions are postulated to account for the formation of the hydroxyalkyl amide VII. Since hydroxyalkyl amides decompose to aldehydes and primary amines,[8] VII is believed to be the precursor of hexanamide and *n*-valeraldehyde found in photoöxidation products from N-pentylhexanamide. Reaction 4 is a transformation that has long been recognized to occur. The radical formed would be expected to stabilize itself by abstraction of a hydrogen atom from the most labile positions available, which would suggest reaction 5 as the next step. Decomposition of hydroperoxy radicals to alkoxy and hydroxyl radicals as proposed in reaction 6 has many analogies.[9] As shown in reaction 8, VII could be formed as a result of abstraction of a hydrogen atom by the alkoxy radical from a neighboring amide molecule. Addition of reactions 4 through 9 gives one free amide radical from the initiation steps reacting with one molecule of oxygen and three molecules of amide to form three amide free radicals and one molecule each of water, primary amide and aldehyde.

Experimental

N-Pentylhexanamide (V).—Pentylamine (87 g., 1 mole) and freshly distilled hexanoic acid (116 g., 1 mole) were dissolved in 200 ml. of xylene and the resultant reaction mixture was heated under reflux for 40 hours. Water (18 ml.) was removed continuously as formed. The reaction mixture was then washed consecutively with 5% sodium hydroxide, 5% hydrochloric acid and water. The xylene solution was dried with magnesium sulfate and evaporated *in vacuo*. The residue, which crystallized when cooled to room temperature, amounted to 156 g. (84%) and melted at 37.5°. It was purified by recrystallization from petroleum ether at −50° to obtain spectroscopically pure N-pentylhexanamide, $k = 126 \times 10^{-4}$ at 2500 A., 4×10^{-4} at 2800 Å., 1.6×10^{-4} at 3000 Å., 0.8×10^{-4} at 3200 A., and 0.0 at 3300 Å.

Anal. Calcd. for $C_{11}H_{23}NO$: C, 71.35; H, 12.43; N, 7.57. Found: C, 71.12; H, 12.51; N, 7.52.

N-Pentylhexanamide-1-C^{14}.—Sodium hexanoate-1-C^{14} was obtained from the Oak Ridge National Laboratory on authorization from the Isotopes Division, U.S. Atomic Energy Commission. This sample, which had an activity of about 1 millicurie, was added to a solution prepared by neutralizing 24 g. of redistilled hexanoic acid with 20% sodium hydroxide. The hexanoic acid was recovered by acidification and extraction with methylene chloride. It was diluted again by addition of 25 g. of hexanoic acid and converted to hexanoyl chloride. Reaction of pentylamine with this acid chloride gave 66 g. (85%) of N-pentylhexanamide-1-C^{14}, m.p. 37.5°, not depressed when mixed with pure inactive amide.

Anal. Calcd. for $C_{11}H_{23}NO$: N, 7.57. Found: N, 7.31, 7.92.

Hexanoic Acid-2-C^{14}.—Sodium valerate-1-C^{14} of about 2 millicuries activity, also obtained from the Oak Ridge National Laboratory on authorization from the Isotopes Division, U.S. Atomic Energy Commission, was added to a solution formed by neutralizing 10 g. of valeric acid with 20% sodium hydroxide. The resultant solution was extracted with methylene chloride to remove non-acidic impurities. It was acidified with hydrochloric acid and again extracted with methylene chloride. The extract was added to 80 g. of valeric acid and the whole distilled at 100° (28 mm.). The radioactive valeric acid was reduced with lithium aluminum hydride according to the method of Brown[10] to obtain 38.4 g. (59%) of 1-pentanol-1-C^{14}, b.p. 136–137.5°. The alcohol was converted to 1-bromopentane-1-C^{14} by reaction with hydrobromic acid.[11] The yield was 81.7 g. (73.5%), b.p. 125–128°. A mixture of the 1-bromopentane-1-C^{14}, sodium cyanide (32.5 g., 0.68 mole), water (42 ml.) and alcohol (82 ml.), was heated under reflux for 30 hours. After cooling and removal of sodium bromide by filtration, the residue was hydrolyzed with aqueous sodium hydroxide and 51.7 g. (82%) of hexanoic acid-2-C^{14}, b.p. 96–98.5° (10 mm.), obtained.

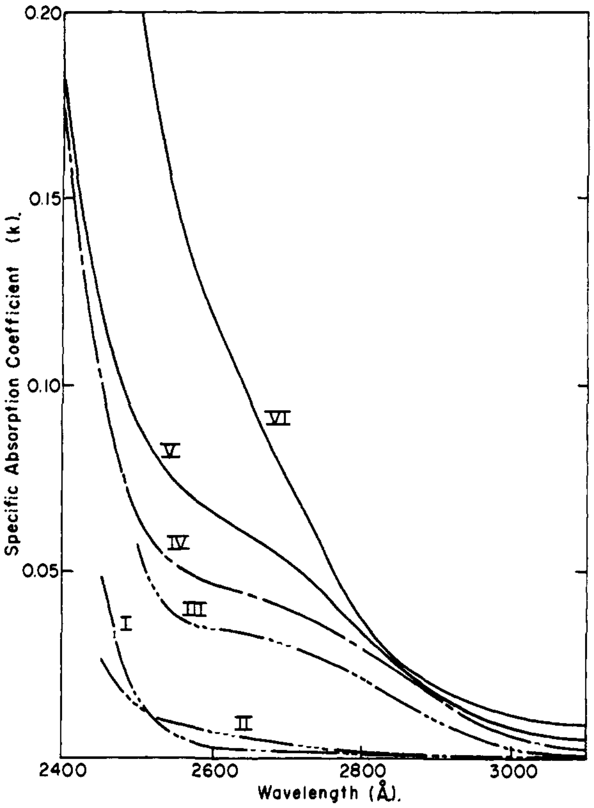


Fig. 1.—Ultraviolet spectrum of amides after exposure: I, N-(1,1-dimethylpropyl)-valeramide; II, N-(1-methylpropyl)-hexanamide; III, N-(2,2-dimethylpropyl)-hexanamide; IV, N-pentyl-2,2-dimethylbutyramide; V, N-pentylhexanamide; VI, N-methyl-N-ethylhexanamide.

N-Pentylhexanamide-2-C^{14}.—A mixture of the above acid (0.45 mole), pentylamine (43.5 g., 0.50 mole) and toluene (100 ml.) was heated under reflux. Water (8 ml., 0.44 mole) was collected as formed. After removal of toluene, the residual amide was purified as described above, m.p. 37–38°, not depressed upon mixture with inactive amide. The yield was 72 g. (87%).

Pentylamine-1-C^{14}.—Sodium cyanide-C^{14} (2 millicuries, obtained from Tracerlab on authorization from the Isotopes Division, U.S. Atomic Energy Commission) was diluted with 37.6 g. of inactive sodium cyanide and allowed to react with 100 g. of *n*-butyl bromide using the method of Adams and Marvel.[12] The yield of valeronitrile was 35.3 g. (58.5% based upon sodium cyanide), b.p. 138–142°. This was

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[8] J. F. Walker, "Formaldehyde," second edition, Reinhold Publishing Corp., New York, N. Y., 1953, p. 291.

[9] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 91.

[10] W. G. Brown, "Organic Reactions," John Wiley and Sons Inc., New York, N. Y., 1951, Vol. VI, p. 486.

[11] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1946, Coll. Vol. 1, p. 27.

[12] R. Adams and C. S. Marvel, THIS JOURNAL, **42**, 310 (1920).

diluted by addition of 25 g. of inactive valeronitrile, which reduced the activity to about 0.84 millicurie per mole.

The radioactive valeronitrile (60 g., 0.7 mole), 30 g. of ammonia (1.8 moles) and 5–10 g. of Raney cobalt were placed in a shaker tube and pressured to 2500 lb./sq. in. with hydrogen. The temperature was increased gradually to 120–125° and kept at that level for 1.5 hours. The total pressure drop was 1800 lb./sq. in., which corresponds to 1.5 moles of hydrogen. From the reaction mixture there was recovered 40.2 g. (64%) of pentylamine-1-C^{14}, b.p. 105°.

N-Pentyl-1-C^{14}-hexanamide.—Pentylamine-1-C^{14} (40 g., 0.46 mole) and hexanoic acid (59 g., 0.51 mole) were allowed to react in 200 ml. of toluene as described above. The yield of pure amide was 66 g. (77.5%).

Anal. Calcd. for $C_{11}H_{23}NO$: N, 7.57. Found: N, 7.48, 7.46.

N-(1,1-Dimethylpropyl)-valeramide (I).—A modification of the method of Ritter and Minieri[13] was employed. Sulfuric acid (250 g.) was added dropwise with stirring to a mixture of valeronitrile (166 g., 2 moles) and 2-methyl-2-butanol (250 g., 2.82 moles) cooled to 10–15°. After addition was complete, the reaction mixture was stirred for 16 hours at room temperature and then poured onto ice. The water-insoluble oil that separated was washed first with water and then with sodium bicarbonate solution. After drying with magnesium sulfate the product was distilled. The fraction boiling at 88–89° (1 mm.), (214 g., 63% yield), $n^{25}D$ 1.4461, d^{25}_4 0.8656, was collected as pure N-(1,1-dimethylpropyl)-valeramide; ultraviolet absorption spectra: $k = 114 \times 10^{-4}$ at 2500 Å., 7×10^{-4} at 2800 Å., 3×10^{-4} at 3000 Å., 0 at 3200 Å.

Anal. Calcd. for $C_{10}H_{21}NO$: C, 70.58; H, 12.28; N, 8.19. Found: C, 70.30; H, 12.34; N, 8.05.

N-(1-Methylpropyl)-hexanamide (II).—*sec*-Butylamine (90 g., 1.23 moles) and hexanoic acid (144 g., 1.30 moles) were dissolved in 200 ml. of toluene. This mixture was heated under reflux and water (20 ml.) was removed as formed. Toluene was removed by distillation at room temperature under reduced pressure and the residue was washed with 5% hydrochloric acid, 5% sodium hydroxide and finally with water. The organic layer then was dried with potassium carbonate and distilled. The fraction boiling at 90–93.5° (0.35 mm.) was collected as N-(1-methylpropyl)-hexanamide (139 g., 81% yield). Redistillation gave a pure fraction boiling at 93° (0.35 mm.), $n^{25}D$ 1.4434, d^{25}_4 0.8656; ultraviolet spectra: $k = 42 \times 10^{-4}$ at 2500 Å., 12×10^{-4} at 2800 Å., 7×10^{-4} at 3000 Å., and 2×10^{-4} at 3300 Å.

Anal. Calcd. for $C_{10}H_{21}NO$: C, 68.79; H, 12.10. Found: C, 68.95; H, 12.22.

N-(2,2-Dimethylpropyl)-hexanamide (III).–2,2-Dimethylpropylamine (50 g., 0.57 mole) and hexanoic acid (70 g., 0.60 mole) were dissolved in 200 ml. of toluene and heated under reflux. Water was removed as formed until 10.5 ml. had been collected. Toluene was removed by distillation and the amide remaining was washed with 10% sodium hydroxide and then with water. Distillation of the amide gave 72.5 g. (68% yield), b.p. 97–98° (0.28 mm.). Redistillation gave pure amide, b.p. 100° (0.45 mm.), $n^{25}D$ 1.4450, d^{25}_4 0.8656; ultraviolet spectra: $k = 27 \times 10^{-4}$ at 2500 Å., 9×10^{-4} at 2800 Å., 5×10^{-4} at 3000 Å., and 1×10^{-4} at 3200 Å.

Anal. Calcd. for $C_{11}H_{23}NO$: C, 71.35; H, 12.43; N, 7.57. Found: C, 71.38; H, 12.55; N, 7.58.

N-Pentyl-2,2-dimethylbutyramide (IV).—To 2,2-dimethylbutyroyl chloride (53 g., 0.39 mole) dissolved in ether was added an ether solution of pentylamine (75 g., 0.99 mole) dropwise. After 24 hours the reaction mixture was filtered to remove pentylamine hydrochloride and the filtrate was washed with 5% hydrochloric acid and then with water. After drying with magnesium sulfate, ether was removed and the residue distilled. The fraction boiling at 102–103° (1 mm.) (42 g., 58% yield) was N-pentyl-2,2-dimethylbutyramide, $n^{25}D$ 1.4476, d^{25}_4 0.8772; ultraviolet spectra: $k = 360 \times 10^{-4}$ at 2500 Å., 10×10^{-4} at 2800 Å., 2×10^{-4} at 3200 Å.

Anal. Calcd. for $C_{11}H_{23}NO$: C, 71.35; H, 12.43; N, 7.57. Found: C, 71.41; H, 12.57; N, 7.58.

N-Methyl-N-ethylhexanamide (VI).—Hexanoyl chloride (85 g., 0.63 mole) was added dropwise to a mixture of methylethylamine hydrochloride (60 g., 0.63 mole) and sodium hydroxide (50 g., 1.26 moles) in 150 ml. of water while cooling in ice. After reaction was complete the organic layer was separated and washed first with 5% hydrochloric acid and then with water. The product was dried with anhydrous magnesium sulfate and distilled to give 59 g. (60% yield) of a pale yellow amide, b.p. 108–110° (10 mm.). Colorless N-methyl-N-ethylhexanamide, b.p. 115° (15 mm.), $n^{25}D$ 1.4443, d^{25}_4 0.8821, was obtained by two additional fractional distillations; ultraviolet spectra: $k = 450 \times 10^{-4}$ at 2500 Å., 22×10^{-4} at 2800 Å., 8×10^{-4} at 3000 Å., and 3×10^{-4} at 3200 Å.

Anal. Calcd. for $C_9H_{19}NO$: C, 68.79; H, 12.10. Found: C, 68.95, 68.88; H, 12.22, 12.25.

Ultraviolet Exposure of N-Pentylhexanamide.—The amide was exposed in a Pyrex glass cell 30 mm. in diameter and 60 mm. in length. The cell contained a side arm large enough to admit a small glass-covered magnetic stirrer bar, a thermocouple well, and a water jacket. This vessel was designed for irradiation from the top through a window of optically flat Pyrex glass. To the vessel was added 10 g. (0.054 mole) of N-pentylhexanamide together with a glass-covered magnetic stirrer bar. It was then connected to a gas buret. The amide was melted, degassed, and then frozen by immersion of the cell in a solid carbon dioxide–acetone mixture. Air in the system was replaced with oxygen by evacuation followed by admission of oxygen of known purity. The cooling mixture was removed and water at 50° from a thermostat was circulated through the jacket. As soon as the amide melted, stirring was started and the lamp turned on. The ultraviolet source was a Hanovia analytic model lamp with a type L burner placed 25 cm. from the surface of the sample. The progress of the photoöxidation was followed by measuring oxygen consumption. During these exposures the temperature of the amide was 51–52°. Similarly, 10-g. samples of each of the amides described in Table IV were exposed for 285 hours at 50°.

Samples of gaseous products were obtained by interposing a gas collecting tube between the exposure vessel and the gas buret. The composition of the gas over the reaction mixture after exposure is given in Table II.

Analysis of Products.—Acids present in exposed amide were neutralized with excess 20% sodium hydroxide. Nonacidic materials were removed by exhaustive continuous extraction with methylene chloride. The aqueous solution was acidified with phosphoric acid and steam distilled. Volatile acids were obtained from the distillate by methylene chloride extraction. Acidic products were obtained by distillation of the extract. Titration demonstrated that negligible amounts of acids were lost during removal of the methylene chloride. Hexanoic and valeric acids were separated by partition chromatography according to the procedure of Ramsey and Patterson.[5] The hexanoic acid recovered from the chromatogram formed an anilide, m.p. 91–93°, that showed no depression in melting point when mixed with authentic hexananilide. The valeric acid isolated from the chromatogram also was converted to an anilide, m.p. 51–54°, mixed m.p. with authentic valeranilide 51–56°. C_1–C_4 monobasic acids were determined by the partition chromatographic method of Marvel and Rands.[6]

Aldehydes were isolated by modification of the exposure apparatus to permit continuous passage of oxygen through the amide during irradiation. Exit gases were passed into a trap containing 20 ml. of 2,4-dinitrophenylhydrazine reagent.[14] During the course of the exposure 2,4-dinitrophenylhydrazones were formed in the trap. The total precipitate obtained after 285 hours of exposure amounted to 750 mg., about half of which was unchanged 2,4-dinitrophenylhydrazine. Chromatographic separation of the phenylhydrazones by the method of Roberts and Green[7] gave the five fractions described in Table I. These derivatives were recovered from the respective fractions by evaporation of the eluting solvents. Amounts of aldehydes present were estimated from recovery of the phenylhydrazones. The identity of these derivatives was established by the correspondence of their X-ray diffraction patterns to patterns given by authentic samples.

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Exposed samples of N-pentylhexanamide were extracted with water and the extract evaporated to dryness. The low-melting residue was recrystallized from isoöctane to obtain white crystals melting at 88–90° (hexanamide melts at 97–98°). The identity of these crystals as hexanamide was established by the exact correspondence of the X-ray diffraction pattern obtained from them with that given by authentic hexanamide.

Addition of 10% sodium hydroxide solution to photo-oxidized N-pentylhexanamide caused evolution of sufficient amounts of either ammonia or an amine to be detected by litmus paper. Quantitative estimation by the ninhydrin procedure and by the method of Van Slyke and Cullen[15] established that less than 2 mg. of ammonia was formed upon exposure of 10 g. of N-pentylhexanamide for 285 hours. Qualitative tests for hydroxylamine and hydrazine[16] were negative. Infrared spectra of irradiated N-pentylhexanamide and of the residual amide after acids had been removed showed no indication of nitriles.

Gas samples were analyzed by the Orsat procedure using a Burrell build-up laboratory model analyzer. Carbon dioxide, oxygen and unsaturated hydrocarbons were determined by usual absorbing reagents. Hydrogen and carbon monoxide were determined by combustion over hot copper oxide in the normal way. Oxygen was added and paraffin hydrocarbons were burned to carbon dioxide over platinized silica at 500°. Inert residual gas was reported as nitrogen. Identity of the inert gas was verified by mass spectrometric analysis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRANDEIS UNIVERSITY]

Some Light Induced Reactions with Disulfide and Mercaptan

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Thiyl radicals from α-thioglycerol and from sun lamp irradiation of bis-(2,2′-carboxyphenyl) disulfide (II) failed to abstract hydrogen from acetic acid or an electron from acetate anion, and irradiated II failed to undergo intramolecular hydrogen or electron transfer. On irradiation, II was reduced to thiosalicylic acid I by ethanol and 2-propanol, and compound I was oxidized to II by acetone. Pinacol appeared to be the major product of oxidation of 2-propanol by di-*n*-butyl disulfide and of reduction of acetone by thiosalicylic acid. Disulfide II was not reduced under our conditions by *t*-butyl alcohol, diisopropyl ether, isopropyl acetate, benzene, toluene, chloroform and lactic acid, but appeared to be reduced by ethyl lactate, leading to ethyl pyruvate. The course of these reactions is discussed.

In the course of our study of the exchange of diphenylmethyl radical, produced from azo-bis-diphenylmethane, with diphenylmethane, we have observed[2] catalysis of this process by thiophenol by the reversible process 1. Conditions were

$$(C_6H_5)_2CH\cdot + C_6H_5SH \underset{b}{\overset{a}{\rightleftarrows}} (C_6H_5)_2CH_2 + C_6H_5S\cdot \qquad (1)$$

found under which approximately half of the diphenylmethyl radicals which became free reacted with mercaptan (reaction 1a) before dimerizing or reacting with thiyl radical, while approximately one-fourth of the thiyl radicals so formed abstracted α-hydrogen from solvent diphenylmethane (reaction 1b) before dimerizing or reacting with diphenylmethyl. It seemed desirable to review and investigate hydrogen transfer reactions of mercaptans and thiyl radicals.

Mercaptans are oxidized by a variety of reagents, including organic free radicals,[3] the first product normally isolated being the disulfide. The transient thiyl radicals may, before entering into radical combination processes, act as hydrogen abstracting agents. Thiyl radicals, formed by reaction of 2-cyano-2-propyl radicals with mercaptans,[3] oxidize 9,10-dihydroanthracene to a derivative of 9,9′-dianthranyl,[4] an aliphatic azo compound to an azine,[4] and a disubstituted hydrazine to an aliphatic azo compound.[5] They may also abstract hydrogen from the carbonyl carbon of aldehydes, catalyzing their decarbonylation,[6] leading in this case to chain reactions.

The disulfides are also very reactive, undergoing rupture of the S–S linkage under acidic[7a,b] and basic[7a,c] catalysis and by radical dissociation.[8a,b] The dissociation into thiyl radicals may be thermal, at elevated temperature,[9a] and this may be facilitated by radical-type initiators,[9b] or it may be induced by light. Diisoamyl disulfide, presumably acting by formation of thiyl radicals, aromatizes tetralin and ionene,[9b] and diphenyl disulfide aromatizes[10] tetralin and other hydroaromatics at 260° and is reduced by cyclohexene at 140°. The photolysis of disulfides initiates the polymerization of styrene,[11] catalyzes the addition of mercaptans to olefins[12] and converts diphenylmethane to tetraphenylethane.[2] Disulfides in

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