ethanol was hydrogenated over 5% palladium on carbon at approximately 40 p.s.i.g. of hydrogen. The product, 10 g. (83%), boiled at 95° at 70 mm.

Anal. Calcd. for $C_6H_{15}NO$: C, 61.49; H, 12.90; N, 11.95. Found: C, 61.53; H, 12.92; N, 11.85.

Acknowledgment.—The microanalyses were performed by Messrs. William Brown, Howard Hunter, George Maciak, David Cline, and Alfred Brown. Many of the starting materials were prepared in this laboratory by Dr. Dwight Morrison and Mr. Lawrence White. The infrared and n.m.r. spectra were obtained by Mr. John Klemm, Mrs. Doris Stephens, and Miss Martha Hofmann. The authors wish to thank especially Dr. Harold Boaz and Messrs. Paul Landis and Donald Woolf, Jr., for their invaluable services in interpreting and compiling the infrared and n.m.r. data.

The Light-Induced Amidation of Terminal Olefins[1]

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The light-induced amidation of terminal olefins with formamide is described. The reaction can be performed both directly and through photochemical initiation by acetone. Yields of up to 90% of the 1:1 adducts are obtained.

Free-radical addition reactions to olefins are widely known in the literature.[3] These reactions have been found to involve a variety of reagents, including acetic, malonic, acetoacetic, and cyanoacetic esters.[4] The reactions are usually induced by initiators (mainly peroxides) or photochemically. Kharasch, Urry, and Kuderna[5] have shown that the addition of aldehydes to olefins to give the derived ketones can be induced by peroxides or light. This reaction, following the general scheme proposed for such additions, is described as a free-radical chain reaction. Similarly, methyl formate reacts with olefins in the presence of peroxides to give 1:1 adducts and higher telomers.[6] Urry and Juveland[7] have shown that amines add to olefins to give higher homologous amines derived by the substitution of alkyl groups for the hydrogen α to the amine group. Friedman and Shechter[8] found that substituted formamides undergo similar reactions with olefins in the presence of peroxides to give products resulting from the addition of both $\cdot CON(CH_3)_2$ and $HCON(CH_3)\dot{C}H_2$ radicals to the olefin.

A study of the addition of formamide to olefins was undertaken with the aim of finding a new process for converting olefins to higher amides, and possibly further to amines by reduction or by use of the Hofmann reaction. Since hydrolysis of the amides to the corresponding carboxylic acids can be effected by standard procedures, this reaction provides a new process for carboxylation of olefins under mild conditions at room temperature. Formamide, besides being a common reagent, has the advantage that its 1:1 adducts with olefins are highly crystalline solids which can be readily isolated.

Results

The light-induced addition of formamides to terminal olefins has been reported by us in a preliminary communication.[9] We have since found that the reaction can be initiated photochemically by acetone, and the present paper includes full details of the reactions and the products obtained.

Formamide was found to add to olefins under photochemical conditions to give mainly the 1:1 adducts resulting from anti-Markovnikov addition.

$$RCH{=}CH_2 + H{-}CONH_2 \xrightarrow{h\nu} RCH_2CH_2CONH_2$$

$$R = \text{alkyl, } H_3COOC(CH_2)_2\text{-, } H_2NOC(CH_2)_2\text{-, } H_3COOC(CH_2)_8\text{-, } H_2NOC(CH_2)_8\text{-}$$

The acetone-initiated reactions produced even higher yields of these adducts and require shorter irradiation periods. The reactions studied and the main products obtained are summarized in Table I. The 1:1 adducts

TABLE I

ADDITION PRODUCTS OF FORMAMIDE AND OLEFINS[a]
(Initiated by Acetone)

Olefin	Product, 1:1 adduct (%)	Source of light
1-Hexene	Heptanamide (50)[b]	Sun
1-Heptene	Octanamide (57)	Sun
	(61)	Ultraviolet[c]
1-Octene	Nonanamide (62)	Sun
	(51)	Ultraviolet[c]
1-Decene	Undecanamide (67)	Ultraviolet[c]
Methyl 10-undecylenate	Methyl 11-carbamoylundecanoate (53)	Ultraviolet[c]
10-Undecylenamide	Dodecanediamide (90)	Sun
Methyl 4-pentenoate	Methyl 5-carbamoylpentanoate (61)	Sun
	(58)	Ultraviolet[c]
4-Pentenamide	Adipamide (77)	Sun

[a] The mole ratio of formamide–olefin in the experiments mentioned was 18:1. [b] Yields are based on the olefins employed. The conversions are nearly quantitative in most cases. [c] Hanau Q81 high pressure mercury vapor lamps fitted into Pyrex tubes were used as the radiation source for these acetone-initiated reactions.

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[2] In partial fulfillment of the requirements for a Ph.D. degree submitted to The Weizmann Graduate School in the Natural Sciences, 1962.

[3] For reviews see (a) J. I. G. Cadogen and D. H. Hey, *Quart. Rev.* (London), **8**, 308 (1954); (b) J. I. G. Cadogen, *Roy. Inst. Chem.* (London), *Lectures*, Monographs, Reports, No. 6 (1961).

[4] (a) J. C. Allen, J. I. G. Cadogen, B. W. Harris, and D. H. Hey, *J. Chem. Soc.*, 4468 (1962); (b) J. C. Allen, J. I. G. Cadogen and D. H. Hey, *Chem. Ind.* (*London*), 1621 (1962).

[5] M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

[6] W. H. Urry and E. S. Huyser, *J. Am. Chem. Soc.*, **75**, 4876 (1953).

[7] W. H. Urry and O. O. Juveland, *ibid.*, **80**, 3322 (1958).

[8] L. Friedman and H. Shechter, *Tetrahedron Letters*, **No. 7**, 238 (1961).

[9] D. Elad, *Chem. Ind.* (*London*), 362 (1962). While our work was in progress, A. Rieche, E. Schmitz, and E. Gründemann [*Angew. Chem.*, **73**, 621 (1961)] reported the addition of formamide to olefins in the presence of peroxides at elevated temperatures.

were identified by their physical properties, elementary analyses, and by comparison with authentic samples. The carbamoyl esters were hydrolyzed to the corresponding dicarboxylic acids which were compared with authentic specimens. In addition, smaller yields of higher telomers were obtained. The 2:1 telomers[10] were characterized by elementary analyses and molecular weights. In the case of propylene, the 2:1 telomer, *i.e.*, 3-methylhexanamide, was compared with an authentic sample. Products resulting from Markovnikov addition of formamide to the olefins were obtained in several cases in low yields. These amides were identified by comparison with authentic samples. Addition products of acetone and the olefins were also isolated and identified by their retention times in gas–liquid chromatography and comparison of their derivatives with authentic specimens.

Discussion

The addition of formamide to terminal olefins can be induced by light directly or initiated photochemically by acetone. In the first case the mixture of the olefin and formamide was homogenized with dry *t*-butyl alcohol and irradiated with the unfiltered light of the source.[11]

It seems that carbamoyl radicals $\cdot CONH_2$ are generated in the mixture either as a result of the collapse of the photoactivated formamide molecule or through hydrogen atom abstraction from formamide by other radicals formed. The olefin serves as a scavenger for the carbamoyl radicals to form the derived amides. The concentration of the carbamoyl radicals so produced seems to be low, and the consumption of olefins is incomplete even after 50 hr. of irradiation, resulting in low yields (~20%) of the 1:1 adducts. In the acetone-initiated reactions, the generation of the carbamoyl radicals seems to be faster and the concentration of these radicals higher. Thus, the addition of formamide to the olefins in the presence of acetone is complete within several hours and high yields of the 1:1 adducts are obtained.[12]

Light filtered through Pyrex (wave length >300 mμ) induces the acetone-initiated reactions, whereas in the absence of acetone very poor yields of the derived amides are obtained.[12b] We therefore assume that the acetone here provides the main light-absorbing system. The carbamoyl radicals $\cdot CONH_2$ are probably generated through abstraction of a hydrogen atom from formamide by the photoactivated acetone molecule.[13] The presence of acetone not only increases the yields of the amides, but also shortens the irradiation periods. Terminal olefins seem to serve as very efficient scavengers for the carbamoyl radicals, since no oxamide is produced during the acetone-initiated reactions if the addition of the olefin and the irradiation periods are controlled.

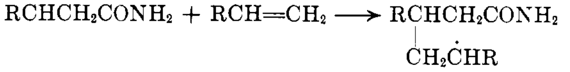
The course of the reaction may be illustrated in the following scheme.

$$\mathrm{H{-}CONH_2} \xrightarrow{h\nu} \mathrm{\cdot CONH_2} \qquad (1)$$

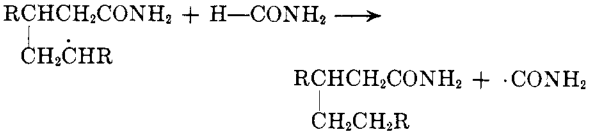
$$\mathrm{H{-}CONH_2} \xrightarrow[\text{acetone}]{h\nu} \mathrm{\cdot CONH_2} \qquad (1a)$$

$$\mathrm{RCH{=}CH_2 + \cdot CONH_2 \longrightarrow R\dot{C}HCH_2CONH_2} \qquad (2)$$

$$\mathrm{R\dot{C}HCH_2CONH_2 + H{-}CONH_2 \longrightarrow RCH_2CH_2CONH_2 + \cdot CONH_2} \qquad (3)$$



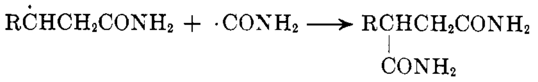
$$\mathrm{R\dot{C}HCH_2CONH_2 + RCH{=}CH_2 \longrightarrow R\underset{\substack{|\\ CH_2\dot{C}HR}}{C}HCH_2CONH_2} \qquad (4)$$



$$\mathrm{R\underset{\substack{|\\ CH_2\dot{C}HR}}{C}HCH_2CONH_2 + H{-}CONH_2 \longrightarrow R\underset{\substack{|\\ CH_2CH_2R}}{C}HCH_2CONH_2 + \cdot CONH_2} \qquad (5)$$

Reactions 1 and 1a (direct light-induced or initiated photochemically by acetone) are the initiation steps, whereas eq. 2 and 3 are the chain propagating steps to form 1:1 adducts. Reactions 4 and 5 lead to 2:1 telomers. Since reactions 3 and 4 compete, the low concentration of the olefin kept throughout the reaction by the slow addition of this reagent leads to high yields of the 1:1 adducts.

Chain termination results, probably, from a variety of reactions. One of the possibilities is the following,



$$\mathrm{R\dot{C}HCH_2CONH_2 + \cdot CONH_2 \longrightarrow R\underset{\substack{|\\ CONH_2}}{C}HCH_2CONH_2}$$

and in fact alkylated succinamides were isolated in some cases (though in poor yields).[14] Higher concentrations of the carbamoyl radicals $\cdot CONH_2$ will favor this reaction; accordingly, the alkylated succinamides were detected only in the reactions irradiated by lamps and not by sunlight, since the concentration of the carbamoyl radicals in the former case is higher.

The experimental observations, *i.e.*, the formation of (a) 1:1 adducts, (b) telomeric products, (c) alkylated succinamides, and (d) oxamide when an olefin is absent, are consistent with a free-radical mechanism. The telomeric products obtained support the assumption of a chain reaction, being characteristic products of this type of reaction.

The point of initial attack in the free-radical addition to olefin of the type $RCH{=}CH_2$ is at the terminal carbon.[3a,b] The intermediate radical (I) produced by this process (anti-Markovnikov) has a higher degree of resonance stabilization than the alternative radical (II). Steric factors also favor the terminal addition. A Markovnikov-like addition was, however, found to take place in the present reaction and amides of the structure $RCH(CH_3)CONH_2$ were isolated in several

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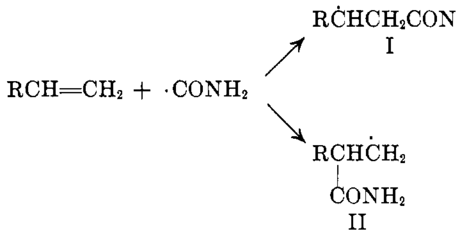
(10) *n*:1 telomer is defined as a molecule formed from *n* molecules of olefin and one molecule of formamide.

(11) Quartz immersion tubes were used for the direct light-induced reactions.

(12) (a) The photolysis of formamide in the absence of an olefin resulted in the formation of oxamide in trace amounts only, whereas the photolysis of formamide in the presence of acetone led to appreciable amounts of oxamide.[12b] (b) Unpublished results from this laboratory.

(13) (a) Because of a lack of accurate physical measurements, the possibility that acetone acts as a photosensitizer and that the generation of the carbamoyl radicals $\cdot CONH_2$ is effected by energy transfer in the triplet states[13b] cannot be excluded. However, our proposed mechanism is supported by the following observations. 2-Methylalkan-2-ols could be isolated from some reaction mixtures. These were probably obtained by addition to the olefin of the ketyl radical $(CH_3)_2\dot{C}OH$ formed by the hydrogen abstraction process. Analogously, a considerable amount of benzpinacol was obtained when benzophenone was used as an initiator.[12b] (b) *Cf.* G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(14) The possibility that oxamide and the alkylated succinamides result from radical addition to formamide cannot be excluded.



cases. The low yields (3–6%) of these amides obtained are in accordance with the view that terminal addition should predominate.[3b,4a]

The addition of acetone to olefins, induced by intiators or light, has been reported recently.[15] Such an addition was found to take place in 5–15% yield (based on olefin) during the present reactions when acetone was used as an initiator. The resulting methyl ketones are assumed to be produced from the addition of acetonyl radicals to the olefin.

$$RCH{=}CH_2 + \cdot CH_2COCH_3 \longrightarrow R\dot{C}HCH_2CH_2COCH_3$$

Experimental[16]

Experiments with ultraviolet light were conducted in an apparatus similar to the one described by de Mayo[17] with slight modifications. Hanau Q81 high pressure mercury vapor lamps fitted into Pyrex immersion tubes were used as the radiation source. The lamp was immersed in the reaction mixture, which was cooled externally with running water, and oxygen-free nitrogen was passed through the mixture throughout the irradiation. The internal temperature was kept at 30–32°.

Reactions in sunlight were performed in Pyrex tubes. The system was flushed with nitrogen after each addition of the olefin.

Reagents.—Formamide, pure grade, was freshly distilled at 0.2 mm. before use; absolute acetone was used; *t*-butyl alcohol was distilled over sodium. Olefins were shaken with aqueous ferrous sulfate solution, dried (Na_2SO_4), and before use were freshly distilled and filtered through a short column of "Alcoa" activated alumina F20. 1-Hexene had b.p. 60°, n^{28}_{D} 1.3832; 1-heptene had b.p. 90–91.5°, n^{25}_{D} 1.3970; 1-octene had b.p. 119–120°, n^{25}_{D} 1.4052; 1-decene had b.p. 166°, n^{28}_{D} 1.4178; methyl 10-undecylenate had b.p. 136–137° (27 mm.), n^{28}_{D} 1.4360; and methyl 4-pentenoate had b.p. 128°, n^{25}_{D} 1.4120.

Typical experiments with ultraviolet light and sunlight are described under A. Other experiments were conducted under similar conditions unless otherwise stated.

A. 1-Heptene and Formamide with Ultraviolet Light.—A mixture of 1-heptene (0.5 g.), formamide (40 g.), *t*-butyl alcohol (35 ml.), and acetone (5 ml.) was irradiated for 45 min. A solution of 1-heptene (4.4 g.), *t*-butyl alcohol (10 ml.), and acetone (7 ml.) was then added in ten equal portions at 45-min. intervals, and irradiation was continued for another 6 hr. After removal of the solvents, formamide was distilled from the mixture at 0.2 mm. Treatment of the residue with acetone and filtration (to remove traces of oxamide), followed by the removal of the solvent and addition of water, led to an oily mixture which was crystallized from acetone–petroleum ether to give 3.2 g. of octanamide, m.p. 98–103°. A pure sample showed m.p. 105–106°, lit.[18] m.p. 105–106°.

The aqueous layer was extracted with chloroform. Treatment of the residue left after removal of the solvent with a small volume of acetone caused the separation of 200 mg. of *n*-pentylsuccinamide, which after crystallization from ethanol exhibited m.p. 218–219°.[19]

An authentic sample was prepared from *n*-pentylsuccinic acid.[20]

Anal. Calcd. for $C_9H_{18}N_2O_2$: C, 58.03; H, 9.74; N, 15.04. Found: C, 57.89; H, 9.98; N, 14.63.

The residue (2.4 g.) from the combined mother liquors was chromatographed on alumina (120 g.). Elution with acetone–petroleum ether (1:9) led to an oil (200 mg.) which is believed to contain a mixture of telomers. Further elution with the same solvent mixture gave a 2:1 telomer (400 mg.), m.p. 63–65° (*n*-pentane).

Anal. Calcd. for $C_{15}H_{31}NO$: C, 74.63; H, 12.94; N, 5.80; mol. wt., 241. Found: C, 74.47; H, 12.90; N, 5.99; mol. wt., 248.

Acetone–petroleum ether (1:9) finally eluted 220 mg. of 2-methylheptanamide. Crystallized from *n*-pentane it showed m.p. 76–77°. An authentic sample was prepared from 2-methylheptanoic acid which had been synthesized by the method of Wilson.[21] Elution with acetone–petroleum ether (3:17) yielded octanamide (850 mg.). Ethanol–acetone (3:7) eluted a glassy oil (640 mg.).

Anal. Found: C, 58.35; H, 10.66; N, 10.58.

The recovered formamide distillate was diluted with saturated aqueous sodium chloride solution and extracted with chloroform. Removal of the solvent gave an oil (1.6 g.) which furnished 320 mg. of octanamide, m.p. 90–94° upon treatment with *n*-pentane. The residue was chromatographed on alumina (70 g.). Petroleum ether eluted 2-decanone (810 mg.), whose 2,4-dinitrophenylhydrazone showed m.p. 73–75° (*n*-pentane), lit.[22] m.p. 73.5–74°.

Elution with benzene–petroleum ether (1:9) gave 2-methylnonan-2-ol (320 mg.). The 3,5-dinitrobenzoate prepared by the method of Brewster and Ciotti[23] showed m.p. 58–60° (petroleum ether).

Anal. Calcd. for $C_{17}H_{24}N_2O_6$: C, 57.94; H, 6.87; N, 7.95. Found: C, 57.70; H, 7.15; N, 8.07.

1-Heptene and Formamide in Sunlight.—A mixture of 1-heptene (1 g.), formamide (40 g.), *t*-butyl alcohol (20 ml.), and acetone (5 ml.) was left in direct sunlight for 1 day, a solution of 1-heptene (3.9 g.), *t*-butyl alcohol (25 ml.), and acetone (5 ml.) was then added in four equal portions at 1-day intervals, and the solution was left in sunlight for another 2 days. It was worked up according to the procedure described above. Treatment of the oily residue with acetone–petroleum ether gave 3.23 g. of crude octanamide, m.p. 82–90°. Crystallization from acetone–petroleum ether gave a pure sample, m.p. 103–105°.

Chromatography of the residue (2.50 g.) from the combined mother liquors on alumina (120 g.) by the procedure described above afforded a mixture of telomers (450 mg.), a 2:1 telomer (400 mg.), 2-methylheptanamide (310 mg.), octanamide (620 mg.), and a glassy oil (680 mg.).

Octanamide (250 mg.), 2-decanone (950 mg.), and 2-methylnonan-2-ol (80 mg.) were isolated from the recovered formamide distillate in the usual manner as described above.

B. 1-Octene and Formamide with Ultraviolet Light.—The procedure described under A was followed using 5.6 g. of 1-octene. The usual method of work-up led to 2.9 g. of crude nonanamide, m.p. 82–86°. Crystallization from acetone–petroleum ether gave a pure sample, m.p. 99–100°, lit.[24] m.p. 99°. *n*-Hexylsuccinamide (120 mg.), m.p. 219–221° (ethanol), was isolated in the usual manner.

Anal. Calcd. for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.07; N, 13.99. Found: C, 60.16; H, 10.06; N, 14.23.

Chromatography of the residue from the mother liquors, as described above, led to a mixture of telomers (820 mg.), and a 2:1 telomer (430 mg.), m.p. 64–66° (*n*-pentane).

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[15] (a) W. Reusch, *J. Org. Chem.*, **27**, 1882 (1962); (b) A. Rieche, E. Gründemann, and E. Schmitz, *Angew. Chem.*, **74**, 182 (1962).

[16] Boiling points and melting points are uncorrected. Merck "acid-washed" alumina was used for chromatography. Petroleum ether refers to the fraction with b.p. 60–80°. Thin-layer chromatography was performed on Kieselgel G (Merck, Darmstadt); mixtures of acetone-petroleum ether were used for elution, the spots being developed by spraying with a 1% solution of iodine in chloroform. All organic solutions were dried with anhydrous sodium sulfate before removal of solvent. Gas-liquid chromatography (g.l.c.) was carried out with a "Pye" argon instrument on a 10% Apiezon M-Celite column. All products described, except the telomers, were compared with authentic samples by means of their melting point, mixture melting point, infrared spectra, and thin-layer chromatography. Liquids were characterized by their retention times in g.l.c. Molecular weights were determined by the Rast method. Analyses were carried out in our microanalytical section directed by Mr. R. Heller.

[17] P. de Mayo, "Advances in Organic Chemistry," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 370.

[18] A. W. Hofmann, *Ber.*, **17**, 1406 (1884).

[19] In some experiments the alkylsuccinamides precipitated after the first treatment of the residue from the reaction mixture with acetone (see above).

[20] K. Bernhard and H. Lincke, *Helv. Chim. Acta*, **29**, 1457 (1946).

[21] C. V. Wilson, *J. Am. Chem. Soc.*, **67**, 2161 (1945).

[22] P. J. G. Kramer and H. Van Duin, *Rec. trav. chim.*, **73**, 63 (1954).

[23] J. H. Brewster and C. J. Ciotti, *J. Am. Chem. Soc.*, **77**, 6214 (1955).

[24] W. A. Hofmann, *Ber.*, **15**, 977 (1882).

Anal. Calcd. for $C_{17}H_{35}NO$: C, 75.77; H, 13.09; N, 5.20; mol. wt., 269 Found: C, 75.85; H, 13.14; N, 5.40; mol. wt., 259.

Also found were 2-methyloctanamide (110 mg.), m.p. 79–80° (*n*-pentane), lit.[25] m.p. 80.8°; nonanamide (1.0 g.); and a glassy oil (820 mg.) which showed the following analysis.

Anal. Found: C, 68.04; H, 11.34; N, 6.88.

Nonanamide (150 mg.), 2-undecanone (860 mg.), and 2-methyldecan-2-ol (250 mg.) were isolated from the recovered formamide distillate by the usual manner. The 2,4-dinitrophenylhyrazone of the ketone showed m.p. 63–64° (*n*-pentane), lit.[22] m.p. 64.5–65°. The 3,5-dinitrobenzoate of the tertiary alcohol exhibited m.p. 47–48° (petroleum ether).

Anal. Calcd. for $C_{18}H_{26}N_2O_6$: C, 59.00; H, 7.15; N, 7.67. Found: C, 59.00; H, 7.15; N, 7.65.

1-Octene and Formamide in Sunlight.—The procedure described under A was followed using 5.6 g. of 1-octene; the mixture was worked up in the usual way. The crude nonanamide obtained (3.75 g.) melted at 92–96°.

The residue from the mother liquors was chromatographed on alumina to yield a mixture of telomers (100 mg.), a 2:1 telomer (430 mg.), 2-methyloctanamide (400 mg.), nonanamide (1 g.), and a glassy oil (840 mg.).

Nonanamide (150 mg.), 2-undecanone (530 mg.), and 2-methyldecan-2-ol (170 mg.) were isolated from the recovered formamide distillate.

C. 1-Decene and Formamide with Ultraviolet Light.—Seven grams of 1-decene were used for this experiment. The usual manner of work-up led to 5.45 g. of crude undecanamide, m.p. 80–85°. Crystallization from acetone–petroleum ether gave a pure sample, m.p. 99–100°, lit.[26] m.p. 103°. *n*-Octylsuccinamide (100 mg.), m.p. 220–222° (ethanol), was obtained by the usual procedure.

Anal. Calcd. for $C_{12}H_{24}N_2O_2$: C, 63.12; H, 10.60; N, 12.27. Found: C, 63.60; H, 10.77; N, 12.13.

Chromatography of the residue from the mother liquors yielded a mixture of telomers (1.21 g.). A pentane solution of the oil left at 0° deposited 200 mg. of a 2:1 telomer, m.p. 60–62° (*n*-pentane).

Anal. Calcd. for $C_{21}H_{43}NO$: C, 77.48; H, 13.32; N, 4.30; mol. wt., 326. Found: C, 76.85; H, 13.28; N, 4.50; mol. wt., 292.

Also found were 2-methyldecanamide (550 mg.), m.p. 81–82° (*n*-pentane), lit.[25] m.p. 81.4°; undecanamide (640 mg.); and a glassy oil (860 mg.) which had the following analysis.

Anal. Found: C, 70.38; H, 11.46; N, 6.69.

Undecanamide (110 mg.) and 2-tridecanone (250 mg.) were isolated from the recovered formamide distillate. The 2,4-dinitrophenylhydrazone of the ketone showed m.p. 68–70° (*n*-pentane), lit.[22] m.p. 70–71°.

D. Methyl 10-Undecylenate and Formamide with Ultraviolet Light.—The general procedure, using 9.9 g. of methyl 10-undecylenate, was followed and led to 3.9 g. of crude methyl 11-carbamoylundecanoate, m.p. 92–95°. Crystallization from acetone–petroleum ether gave a pure sample, m.p. 96–98°, $\nu_{\max}^{CHCl_3}$ 1661 and 1726 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{25}NO_3$: C, 64.16; H, 10.36; N, 5.76. Found: C, 64.17; H, 10.28; N, 5.89.

The product gave dodecanedioic acid upon alkaline hydrolysis.

The aqueous layer was worked up in the usual manner.[27] The residue from the mother liquors was chromatographed on alumina leading to an oil (2.7 g.), crystallization of which from *n*-pentane yielded 2.1 g. of methyl 13-oxotetradecanoate, m.p. 40–41°, lit.[15b] m.p. 38–40°. An authentic sample was prepared by the method of Robinson.[28] The 2,4-dinitrophenylhydrazone melted at 81–83° (ethanol).

Anal. Calcd. for $C_{21}H_{32}N_4O_6$: C, 57.78; H, 7.39; N, 12.84. Found: C, 57.61; H, 7.53; N, 12.95.

A 2:1 telomer (600 mg.) was found and had m.p. 64–66° (acetone–petroleum ether).

Anal. Calcd. for $C_{25}H_{47}NO_5$: C, 67.99; H, 10.73; N, 3.17; mol. wt., 442. Found: C, 67.94; H, 10.63; N, 3.25; mol. wt., 393.

Also found were methyl 11-carbamoylundecanoate (2.55 g.) and a glassy oil (1.1 g.) which showed the following analysis.

Anal. Found: C, 62.92; H, 10.07; N, 5.15.

E. 10-Undecylenamide and Formamide in Sunlight.—A mixture of 10-undecylenamide (2 g.), formamide (40 g.), *t*-butyl alcohol (25 ml.), and acetone (5 ml.) in a Pyrex conical flask stoppered under nitrogen was left in direct sunlight. (A solid started precipitating at the end of the second day.) After 2 days, a solution of 10-undecylenamide (7.15 g.) in *t*-butyl alcohol (55 ml.) and acetone (7 ml.) was added in five equal portions at 2-day intervals, and the mixture was left in sunlight for another 2 days. The precipitate was washed with acetone to yield 9 g. of dodecanediamide, m.p. 172–180°. Crystallization from ethanol gave a pure sample, m.p. 185–187°, lit.[29] m.p. 189°.

The formamide was removed from the filtrate in the usual way. Boiling the residue with acetone left an insoluble material (1.3 g.) which was filtered off rapidly. It melted at 183–185° (ethanol) and was identified as dodecandediamide.

From the filtrate the amide of 13-oxotetradecanoic acid (1.12 g.), m.p. 117–118° (acetone), was obtained.

Anal. Calcd. for $C_{14}H_{27}NO_2$: C, 69.66; H, 11.28; N, 5.80. Found: C, 69.67; H, 11.17; N, 5.98.

The 2,4-dinitrophenylhydrazone showed m.p. 131–132° (ethanol).

Anal. Calcd for $C_{20}H_{31}N_5O_5$: C, 56.99; H, 7.41; N, 16.62. Found: C, 56.70; H, 7.49; N, 16.85.

F. Methyl 4-Pentenoate and Formamide with Ultraviolet Light.—Methyl 4-pentenoate (5.7 g.) was used for the reaction. Saturated aqueous sodium chloride solution was added to the residue obtained in the usual manner, leading to 3.25 g. of crude methyl 5-carbamoylpentanoate, m.p. 82–88°. Crystallization from acetone–petroleum ether gave a pure sample, m.p. 94–96°, $\nu_{\max}^{CHCl_3}$ 1668 and 1724 cm.$^{-1}$.

Anal. Calcd. for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.80. Found: C, 52.85; H, 8.00; N, 8.86.

The product yielded adipic acid upon alkaline hydrolysis. The residue from the mother liquors was chromatographed on alumina to yield a mixture of telomers (660 mg., eluted with acetone–petroleum ether 3:7), methyl 5-carbamoylpentanoate (1.3 g., eluted with acetone–petroleum ether 1:1), and a glassy oil (1.03 g.) which showed the following analysis.

Anal. Found: C, 49.80; H, 7.78; N, 8.25.

Workup of the recovered formamide distillate led to an oil (1.4 g.) which contained a ketone. The 2,4-dinitrophenylhydrazone showed m.p. 83–85° (ethanol) and was identical with the same derivative of methyl 7-oxooctanoate, prepared by the method of Robinson.[28]

Anal. Calcd. for $C_{15}H_{20}N_4O_6$: C, 51.13; H, 5.72; N, 15.90. Found: C, 51.12; H, 5.85; N, 15.80.

Methyl 4-Pentenoate and Formamide in Sunlight.—A yield of 4.3 g. of crude methyl 5-carbamoylpentanoate, m.p. 84–91°, was obtained from 5.7 g. of methyl 4-pentenoate. Chromatography of the residue from the mother liquors led to an additional crop of methyl 5-carbamoylpentanoate (510 mg.).

Work-up of the recovered formamide distillate gave an oil (1.5 g.), from which methyl 7-oxooctanoate was isolated as its 2,4-dinitrophenylhydrazone derivative.

G. 4-Pentenamide and Formamide in Sunlight.—A mixture of 4-pentenamide (1 g.), formamide (40 g.), *t*-butyl alcohol (20 ml.), and acetone (5 ml.) in a Pyrex conical flask stoppered under nitrogen was left in direct sunlight. (Precipitation of the product started at the end of the second day.) After 2 days, a solution of 4-pentenamide (4 g.), *t*-butyl alcohol (50 ml.), and acetone (5 ml.) was added in five equal portions at 2-day intervals, and the mixture was left in sunlight for another 2 days. The precipitate was washed with hot acetone to yield 4.4 g. of adipamide, m.p. 210–215°. Crystallization from ethanol gave a pure sample, m.p. 224–226°, lit.[30] m.p. 220°.

Formamide was removed from the filtrate in the usual way. Treatment of the residue with acetone–ethanol led to the isolation of an additional crop (1.17 g.) of adipamide.

The residue from the mother liquor was treated with water and extracted with chloroform. Removal of the solvent gave a solid

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(25) C. de Hoffmann and E. Barbier, *Bull. soc. chim. Belges*, **45**, 565 (1936).

(26) P. A. Levene and C. J. West, *J. Biol. Chem.*, **18**, 463 (1914).

(27) In some experiments a solid, m.p. 187–189° (acetone), was obtained at this stage by treatment of the residue with a small volume of acetone. *Anal.* Calcd. for $C_{14}H_{26}N_2O_4$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.68; H, 9.28; N, 9.49. The elemental analysis suggests that this compound might be methyl 10,11-dicarbamoylundecanoate, in analogy with other cases.

(28) G. M. Robinson, *J. Chem. Soc.*, 1543 (1934).

(29) C. R. Barnicoat, *ibid.*, 2926 (1927).

(30) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. 1, Eyre and Spottiswoode, London, 1953, p. 33.

(620 mg.), m.p. 90–91° (acetone–petroleum ether), which was identified as the amide of 7-oxooctanoic acid.

Anal. Calcd. for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 60.84; H, 9.51; N, 8.91.

The 2,4-dinitrophenylhydrazone showed m.p. 142–144° (ethanol).

Anal. Calcd. for $C_{14}H_{19}N_5O_5$: C, 49.84; H, 5.68; N, 20.76. Found: C, 49.86; H, 5.85; N, 20.95.

H. 1-Hexene and Formamide in Sunlight.—Heptananide (1.31 g.), m.p. 98–100° (acetone–petroleum ether), lit.[31] m.p. 96°, was obtained from 4.2 g. of 1-hexene. The residue[32] from the combined mother liquors was chromatographed and yielded a mixture of telomers (800 mg.), and a 2:1 telomer (510 mg)., m.p. 67–68° (*n*-pentane).

Anal. Calcd. for $C_{13}H_{27}NO$: C, 73.18; H, 12.76; N, 6.57; mol. wt., 213. Found: C, 73.00; H, 12.78; N, 6.40; mol. wt., 206.

Also found were heptanamide (1.3 g.) and a glassy oil (720 mg.) which had the following analysis.

Anal. Found: C, 64.21; H, 11.60; N, 7.68.

An additional 600 mg. of heptanamide was obtained in the usual manner from the recovered formamide distillate.

I. Propylene and Formamide in Sunlight.—A mixture of propylene (3.5 ml. as liquid), formamide (40 g.), *t*-butyl alcohol (25 ml.), and acetone (15 ml.) was left in direct sunlight in a sealed Pyrex tube for 1 week. After work-up, an oil (1.1 g.) was obtained and was chromatographed on alumina (55 g.) to yield 360 mg. of crude 3-methylhexanamide, m.p 55–60°. Crystallization from acetone–petroleum ether gave a pure sample, m.p. 96–97°, lit.[33] m.p. 97°, and 130 mg. of crude butyramide which was sublimed on a steam bath and showed m.p. 114–116°, lit.[34] m.p. 115°.

J. 1-Octene and Formamide without Acetone.—A mixture of 1-octene (5.6 g.), formamide (40 g.), and *t*-butyl alcohol (55 ml.) was irradiated for 44 hr. (A quartz immersion tube was used for this experiment.) Work-up led to 400 mg. of crude nonanamide, m.p. 90–92°.

The residue from the mother liquors (2.6 g.) was chromatographed on alumina (130 g.) to yield a mixture of telomer (1.0 g.), a 2:1 telomer (350 mg.) which was identical with the 2:1 telomer obtained from the acetone-initiated reaction, nonanamide (710 mg.), and an oil (460 mg.) which had the following analysis.

Anal. Found: C, 69.45; H, 11.48; N, 7.05.

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(31) J. S. Lumsden, *J. Chem. Soc.*, **87**, 90 (1905).

(32) In experiments carried out with ultraviolet light (unpublished results from this laboratory) *n*-butylsuccinamide, m.p. 216–217° (ethanol), was isolated. *Anal.* Calcd. for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.36; N, 16.27. Found: C, 55.97; H, 9.40; N, 16.49.

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(34) W. A. Hofmann, *Ber.*, **15**, 977 (1882).

Ester Formation and Coupling at Phosphorus on Reaction of Diphenylphosphinous Chloride with Diols and Tertiary Amines[1]

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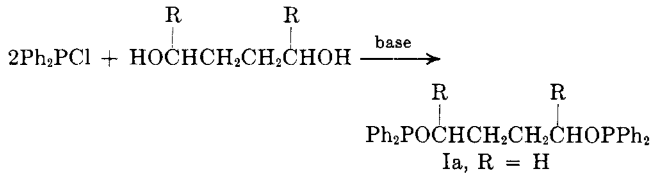
1,4-Butanediol and 2,5-hexanediol reacted smoothly with diphenylphosphinous chloride in the presence of diethylaniline to yield solid bisphosphinites. Ethylene glycol failed to yield a solid bisphosphinite; on distillation the product of the Arbuzov rearrangement of this ester, ethylene bis(diphenylphosphine oxide), was obtained. From the diol reaction mixtures, trace to appreciable amounts of a by-product identified as tetraphenyldiphosphine dioxide were obtained. It was also found that the reaction of ethanol with diphenylphosphinous chloride gave this unusual by-product, apparently not previously observed in such reactions.

Phosphinous chlorides are known to react with alcohols to form phosphinites in the presence of a tertiary amine.[3] We have used this reaction to prepare bisphosphinites, desired for anticancer screening, from certain glycols and diphenylphosphinous chloride.

1,4-Butanediol and 2,5-hexanediol reacted smoothly with diphenylphosphinous chloride in the presence of diethylaniline in ether solution. The bisphosphinites so produced were recovered as low-melting, crystalline solids. Compound Ia showed strong infrared absorption at 1045 cm.$^{-1}$, attributable to the P–O–C group.[4] The spectrum of Ib possessed two medium intensity peaks (1000 and 1055 cm.$^{-1}$) in the P–O–C region.



$$2Ph_2PCl + HO\overset{R}{C}HCH_2CH_2\overset{R}{C}HOH \xrightarrow{\text{base}} Ph_2PO\overset{R}{C}HCH_2CH_2\overset{R}{C}HOPPh_2$$

Ia, R = H
b, R = CH_3

Neither ester exhibited absorption in the phosphoryl region (1175–1250 cm.$^{-1}$), and thus Arbuzov rearrangement to isomeric phosphine oxides had not occurred. In further confirmation of their structures, esters Ia and Ib rapidly decolorized iodine solutions, and on neutral hydrolysis gave diphenylphosphine oxide, identified by its infrared spectrum and by its chloral adduct.[5] Hydrolysis of phosphinites to *sec*-phosphine oxides has been observed previously.[6]

Compound Ia was converted to the known[7] tetramethylene bis(diphenylphosphine oxide) by Arbuzov rearrangement with a small amount of ethyl iodide in refluxing heptane. Phosphoryl absorption for this compound occurred as a singlet at 1177 cm.$^{-1}$; in the spectrum of ethylene bis(diphenylphosphine oxide) (*vide infra*), a doublet at 1170–1180 cm.$^{-1}$ is present. No rearrangement was detected on simply heating Ia at 150–200° for 2 hr. Compound Ib failed to undergo rearrangement in the presence of ethyl iodide in either refluxing heptane or dodecane at 145°.

Attempts to prepare ethylene bis(diphenylphosphinite) (II) have been unsuccessful. A nearly quanti-

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(2) Philip Morris Research Assistant, 1962–1963.

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(6) (a) M. Sander, *Ber.*, **93**, 1220 (1960); (b) M. I. Kabachnik and E. N. Tsvetkov, *Dokl. Akad. Nauk. SSSR*, **135**, 323 (1960).

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