Photoamidation. III.[1] The Light-Induced Amidation of Nonterminal Olefins

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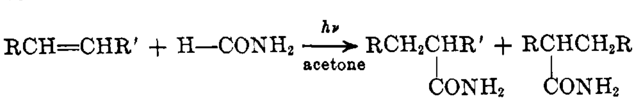
The acetone-initiated photochemical addition of formamide to nonterminal olefins is described. The addition to unsymmetrical olefins results in the formation of two isomeric amides (1:1 adducts) in yields of up to 76%. Methyl oleate and oleamide produce mixtures of the derived amides (1:1 adducts) in yields of up to 74%.

The light-induced amidation of terminal olefins and norbornene with formamide has been described recently.[1] This reaction has been shown to produce high yields of the derived amides resulting from an anti-Markovnikov addition of formamide to terminal double bonds. In the case of norbornene it has been shown to be stereospecific, leading exclusively to the *exo* isomer. A similar addition of formamide to nonterminal double bonds has been found to occur and the present paper includes full details of these reactions and the products obtained.

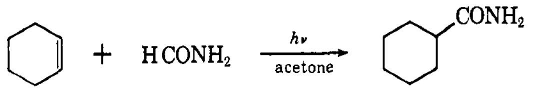
Results

Formamide was found to undergo acetone-initiated photochemical addition[3] to nonterminal olefins to yield mainly a mixture of the derived amides (1:1 adducts). These amides result from addition of a carbamoyl group to either carbon atom of the double bond. Addition of formamide to 2-heptene gave a mixture of the two possible 1:1 adducts, 2-methylheptanamide (2 parts) and 2-ethylhexanamide (1 part). Similarly, the addition of formamide to 2-octene led to 2-methyloctanamide (2 parts) and 2-ethylheptanamide (1 part). The isomeric amides were separated by chromatography on alumina. Methyl oleate and oleamide produced mixtures of the carbamoyl esters and diamides, respectively, as the main products of the reaction. In these cases clean separation could not be achieved.



$$\mathrm{RCH{=}CHR' + H{-}CONH_2 \xrightarrow[\text{acetone}]{h\nu} \underset{\displaystyle CONH_2}{RCH_2CHR'} + \underset{\displaystyle CONH_2}{RCHCH_2R'}}$$

$R = R' = CH_3$; $R = CH_3(CH_2)_3$, $R' = CH_3$;
$R = CH_3(CH_2)_4$, $R' = CH_3$; $R = CH_3(CH_2)_2$, $R' = C_2H_5$;
$R = CH_3(CH_2)_7$, $R' = (CH_2)_7COOCH_3$;
$R = CH_3(CH_2)_7$, $R' = (CH_2)_7CONH_2$



The 1:1 adducts were characterized by means of their physical properties as well as by comparison with authentic samples. The carbamoyl esters and diamides derived from methyl oleate and oleamide were prepared by conventional methods (Experimental Section) and found to be identical with the products obtained from the light-induced reactions. In addition, smaller yields of oils probably higher telomers were obtained in all cases. In the case of cyclohexene, the 2:1 telomer mixture was shown to consist of a mixture of *cis*- and *trans*-bicyclohexyl-2-carboxamide, as evidenced by comparison with authentic samples. The reactions investigated and the main products obtained are summarized in Table I.

Table I

Addition Products of Formamide and Olefins[a]

(Initiated by acetone)

Olefin	Product (1:1 adduct) (%)	Source of light
cis-2-Butene	2-Methylbutyramide (51)[b]	Sun
trans-2-Butene	2-Methylbutyramide (51)	Sun
cis-2-Heptene	2-Methylheptanamide (34) 2-Ethylhexanamide (17)	Ultraviolet[c]
	2-Methylheptanamide (47) 2-Ethylhexanamide (21)	Sun
2-Heptene[d]	2-Methylheptanamide (30) 2-Ethylhexanamide (15)	Ultraviolet[c]
	2-Methylheptanamide (45) 2-Ethylhexanamide (24)	Sun
3-Heptene[e]	2-Ethylhexanamide (32) 2-Propylpentanamide (22)	Ultraviolet[c]
	2-Ethylhexanamide (33) 2-Propylpentanamide (22)	Sun
2-Octene[f]	2-Methyloctanamide (39) 2-Ethylheptanamide (18)	Ultraviolet[c]
	2-Methyloctanamide (50) 2-Ethylheptanamide (27)	Sun
Methyl oleate	Methyl 9-carbamoyloctadecanoate (44) Methyl 10-carbamoyloctadecanoate	Ultraviolet[c]
	Methyl 9-carbamoyloctadecanoate (60) Methyl 10-carbamoyloctadecanoate	Sun
Oleamide	9-Carbamoyloctadecanamide (74) 10-Carbamoyloctadecanamide	Sun
Cyclohexene	Cyclohexanecarboxamide (65)	Ultraviolet[c]
	Cyclohexanecarboxamide (65)	Sun

[a] The mole ratio of formamide–olefin in the experiments mentioned was 18:1 (except for methyl oleate and oleamide). [b] Yields are based on the olefins employed. [c] Hanau Q81 high-pressure mercury-vapor lamps fitted into Pyrex tubes were used as the radiation source for these acetone-initiated reactions. [d] 73% *cis* and 27% *trans*. [e] 67% *cis* and 33% *trans*. [f] 61% *cis* and 39% *trans*.

Addition products of acetone and the olefins were also isolated. In each case they consisted of mixtures of methyl ketones, resulting from the addition of an acetonyl group to either carbon atom of the double bond. These products were identified by comparison of their retention times in gas–liquid chromatography (g.l.c.) with those of authentic samples.

Discussion

Details of the addition reaction of formamide to olefins have been discussed in our previous publica-

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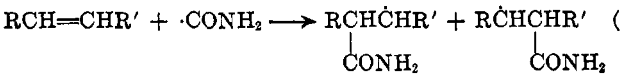
(1) (a) Part I: D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964); (b) part II: D. Elad and J. Rokach, *J. Chem. Soc.*, 800 (1965).

(2) In partial fulfillment of the requirements for a Ph.D. degree submitted to the Feinberg Graduate School of The Weizmann Institute of Science.

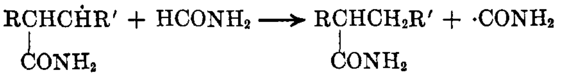
(3) All reported reactions were initiated photochemically with acetone; this method gave higher yields both with nonterminal and terminal olefins.

tion.[1] The free-radical chain mechanism proposed for the addition of formamide to terminal olefins may be extended to include the present cases. As previously suggested,[1] this reaction involves carbamoyl radicals $\cdot\mathrm{CONH_2}$ generated in the irradiated mixture, with the olefin serving as a scavenger for these radicals, thus leading to the derived amides and higher telomers.

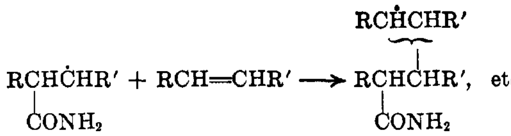
$$\mathrm{HCONH_2} \xrightarrow[\text{acetone}]{h\nu} \mathrm{\cdot CONH_2} \qquad (1)$$



$$\mathrm{RCH{=}CHR' + {\cdot}CONH_2 \longrightarrow R\underset{CONH_2}{C}H\dot{C}HR' + R\dot{C}H\underset{CONH_2}{C}HR'} \qquad (2)$$



$$\mathrm{R\underset{CONH_2}{C}H\dot{C}HR' + HCONH_2 \longrightarrow R\underset{CONH_2}{C}HCH_2R' + {\cdot}CONH_2} \qquad (3)$$



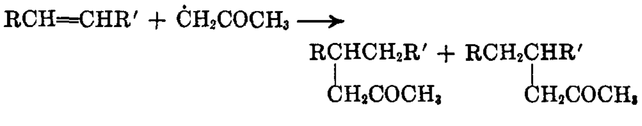
$$\mathrm{R\underset{CONH_2}{C}H\dot{C}HR' + RCH{=}CHR' \longrightarrow R\underset{CONH_2}{C}H\overset{RCH\dot{C}HR'}{C}HR',\ etc.} \qquad (4)$$

The initial attack of the carbamoyl radical on a terminal olefin occurs mainly at the terminal carbon (anti-Markovnikov) leading almost exclusively to a single 1:1 adduct, though the isomeric adduct was produced in small amounts.[1] In unsymmetrical nonterminal olefins the direction of the initial attack of the radical is less specific, thus leading to a mixture of the two possible 1:1 adducts. Our results are compatible with those obtained by Allen, *et al.*,[4] who obtained the same ratio of the corresponding isomers in the free-radical addition of diethyl malonate to 2-octene. These authors attribute their results to steric factors which, most probably, operate in the present case too.[5,6]

The reaction of formamide with cyclohexene led to an addition product, *i.e.*, cyclohexanecarboxamide, rather than a product of substitution at the allylic position. Neither products resulting from the latter reaction nor any formation of bicyclohexenyl could be detected. We assume that the low concentration of cyclohexene in the formamide–acetone mixture may be responsible for the observed path of the reaction. On the other hand, the reactivity of the carbamoyl radicals toward the double bond may also play an important role in the reaction path. De Mayo, *et al.*,[7] have shown that in the photoreaction of aldehydes and cyclohexene, the ratio of addition to substitution varies considerably with the concentration of cyclohexene. The effect of concentration of cyclohexene on its reaction path with formamide is under investigation.

Either *cis* or *trans* olefins or mixtures of the two led to identical addition products with formamide. In each case the over-all yields and ratios of isomeric products were identical. *cis–trans* isomerization of the olefins during the reaction may account for these results.[8] This point, as well as the steric factors involved in the addition of formamide to olefins, are now under investigation with a variety of branched olefins.

The addition of acetone, when used as an initiator, to olefins has been reported by us previously.[1] This addition has been shown to follow the same path as the formamide addition, leading to methyl ketones resulting from "terminal addition" in the case of terminal olefins, and to *exo*-2-acetonylnorbornane in the case of norbornene. In a similar manner, we obtained methyl ketones (in 3–8% yield, based on olefins employed) in the reactions with nonterminal olefins. These ketones are assumed to be produced from the addition of acetonyl radicals to either carbon of the double bond. The ratios of the isomeric methyl ketones were the same as those of the appropriate amides obtained in these reactions.



$$\mathrm{RCH{=}CHR' + \dot{C}H_2COCH_3 \longrightarrow R\underset{CH_2COCH_3}{C}HCH_2R' + RCH_2\underset{CH_2COCH_3}{C}HR'}$$

Experimental Section[9]

Reagents.—2-Heptene had b.p. 97–99°, n^{26}_{D} 1.4020 (73% *cis*, 27% *trans*[10]); *cis*-2-heptene had b.p. 94–96°, n^{31}_{D} 1.4060; 3-heptene had b.p. 94–96°, n^{31}_{D} 1.4000 (67% *cis*, 33% *trans*[10]); 2-octene had b.p. 123–124°, $n^{28.5}_{\mathrm{D}}$ 1.4119 (61% *cis*, 39% *trans*[10]); cyclohexene had b.p. 80–82°, n^{31}_{D} 1.4415; oleamide had m.p. 74–78°; *cis*- and *trans*-2-butene were used without purification.

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

A. 2-Heptene and Formamide. 1. With Ultraviolet Light.—A mixture of 2-heptene (0.5 g.), formamide (40 g.), *t*-butyl alcohol (35 ml.), and acetone (5 ml.) was irradiated for 1 hr. A solution of 2-heptene (4.4 g.), *t*-butyl alcohol (10 ml.), and acetone (3 ml.) was then added in seven equal portions at 1-hr. intervals, and irradiation was continued for another 36 hr. After removal of the solvents, formamide was distilled from the mixture at 0.2 mm., the residue was treated with saturated aqueous sodium chloride solution and extracted with chloroform. Removal of the solvent gave an oil (2.85 g.) which was chromatographed on alumina (150 g.). Elution with acetone–petroleum ether (b.p. 60–80°) (1:19) led to an oil (310 mg.) which is believed to contain a mixture of telomers. Further elution with the same solvent mixture gave 2-ethylhexanamide (630 mg.). Crystallization from acetone–petroleum ether gave a pure sample, m.p. 101–103°, lit.[11] m.p. 101–102°. Acetone–petroleum ether (1:19) finally eluted 1.41 g. of 2-methylheptanamide. Crystallized from *n*-pentane, it showed m.p. 76–78°. An authentic sample was prepared from 2-methylheptanoic acid which was synthesized by the method of Wilson.[12] Elution with ethanol–acetone (4:6) yielded a polar oil (400 mg.).

The recovered formamide distillate was diluted with saturated aqueous sodium chloride solution and extracted with chloroform. Removal of the solvent gave an oil (1.82 g.) which was chromatographed on alumina (90 g.). Petroleum ether eluted an oil (320 mg.) which was shown to consist of 4-methyl-2-nonanone (210 mg.) and 4-ethyl-2-octanone (90 mg.) (g.l.c. at 75°). Acetone–petroleum ether (1:19) eluted first an oil (100 mg.)

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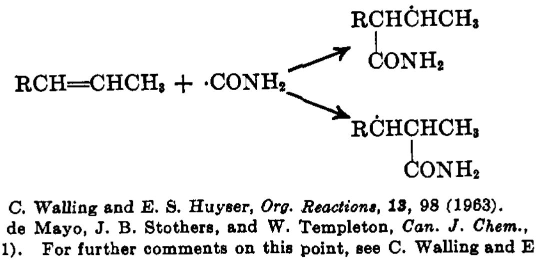
[4] J. C. Allen, J. I. G. Cadogen, B. W. Harris, and D. H. Hey, *J. Chem. Soc.*, 4468 (1962).

[5] The two possible intermediate radicals in the present addition reaction are of approximately equal stability.



$$\mathrm{RCH{=}CHCH_3 + {\cdot}CONH_2 \longrightarrow R\underset{CONH_2}{C}H\dot{C}HCH_3 \ \text{or}\ R\dot{C}H\underset{CONH_2}{C}HCH_3}$$

[6] *Cf.* C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 98 (1963).

[7] P. de Mayo, J. B. Stothers, and W. Templeton, *Can. J. Chem.*, **39**, 488 (1961). For further comments on this point, see C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 101 (1963).

[8] *Cf.* A. C. Testa, *J. Org. Chem.*, **29**, 2461 (1964), and references cited therein.

[9] For general experimental details and description of apparatus, see D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964).

[10] Determined on a 30% silver nitrate–ethylene glycol column. We are indebted to Mr. M. Lachmi for these determinations.

[11] H. S. Raper, *J. Chem. Soc.*, **91**, 1837 (1907).

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

followed by 410 mg. of 2-ethylhexanamide and finally 750 mg. of 2-methylheptanamide.

2. **In Sunlight.**—A mixture of 2-heptene (0.5 g.), formamide (40 g.), *t*-butyl alcohol (20 ml.), and acetone (5 ml.) was left in direct sunlight for 3 days. A solution of 2-heptene (4.4 g.), *t*-butyl alcohol (20 ml.), and acetone (3 ml.) was then added in five equal portions at 5-day intervals, and the mixture was left in sunlight for another 2 weeks. It was worked up according to the procedure described above. Chromatography of the residue (4.73 g.) on alumina (250 g.) afforded a mixture of telomers (270 mg.), 2-ethylhexanamide (1.0 g.), 2-methylheptanamide (2.12 g.), and a polar oil (1.18 g.). The usual work-up of the formamide distillate gave 410 mg. of a mixture of 4-methyl-2-nonanone (260 mg., g.l.c.), 4-ethyl-2-octanone (150 mg., g.l.c.), 2-ethylhexanamide (740 mg.), and 2-methylheptanamide (1.12 g.).

B. *cis*-2-Heptene and Formamide. 1. With Ultraviolet Light.—The quantities and experimental conditions described under A were followed. The residue (3.7 g.) obtained by the usual work-up was chromatographed on alumina (185 g.) to yield a mixture of telomers (430 mg.), 2-ethylhexanamide (830 mg.), 2-methylheptanamide (1.65 g.), and a polar oil (700 mg.). 4-Methyl-2-nonanone (260 mg., g.l.c.), 4-ethyl-2-octanone (140 mg., g.l.c.), 2-ethylhexanamide (420 mg.), and 2-methylheptanamide (800 mg.) were obtained from the recovered formamide distillate.

2. **In Sunlight.**—The procedure described under A, using similar quantities, was followed. Excess of solvents were removed under water pump vacuum, and saturated aqueous sodium chloride solution was then added to the residue followed by extraction with chloroform. Removal of the chloroform led to a residue (6.4 g.) which was chromatographed on alumina (320 g.) to yield 720 mg. of a mixture of 4-methyl-2-nonanone (460 mg., g.l.c.) and 4-ethyl-2-octanone (260 mg., g.l.c.) eluted with petroleum ether, a mixture of telomers (310 mg.), 2-ethylhexanamide (1.52 g.), and 2-methylheptanamide (3.35 g.) eluted with acetone–petroleum ether (1:19), and finally a polar oil (420 mg.) eluted with ethanol–acetone (3:7).

C. 3-Heptene and Formamide. 1. With Ultraviolet Light.—The quantities and experimental conditions described under A were followed and irradiation was continued for 60 hr. The residue (3.6 g.) obtained by the usual work-up was chromatographed on alumina (180 g.) to yield a mixture of telomers (220 mg.) eluted with acetone–petroleum ether (1:9), and 2.72 g. of a mixture of 2-ethylhexanamide and 2-propylpentanamide. The mixture showed m.p. 94–100°.[13] Ethanol–acetone (2:3) eluted a polar oil (500 mg.). Work-up of the recovered formamide led to a residue (1.7 g.) which was chromatographed on alumina (85 g.) to yield 150 mg. of a mixture of 4-ethyl-2-octanone (90 mg., g.l.c. at 75°) and 4-propyl-2-heptanone (60 mg., g.l.c. at 75°) eluted with petroleum ether, and a mixture of 2-ethylhexanamide and 2-propylpentanamide (1.19 g.) eluted with acetone–petroleum ether (1:9).

One gram of the total amide mixture was heated under reflux (nitrogen) with potassium hydroxide (5 g.) in ethylene glycol (20 ml.) for 3 days. The mixture of acids obtained was esterified with diazomethane and the resulting ester mixture was shown by g.l.c.[14] to consist of methyl 2-ethylhexanoate (60%) and methyl 2-propylpentanoate (40%).

2. **In Sunlight.**—The quantities described under A were used and the mixture was left in sunlight for 65 days and worked up as described under B in sunlight. The residue (5.7 g.) was chromatographed on alumina (330 g.) to give 370 mg. of a mixture of 4-ethyl-2-octanone (220 mg., g.l.c.) and 4-propyl-2-heptanone (150 mg., g.l.c.), 500 mg. of a mixture of telomers, a mixture of 2-ethylhexanamide and 2-propylpentanamide (4 g.), and a polar oil (740 mg.).

D. 2-Octene and Formamide. 1. With Ultraviolet Light. – The general procedure described under A was followed using 5.6 g. of 2-octene. The residue (4.2 g.) was chromatographed on alumina (210 g.) to give a mixture of telomers (460 mg.); 2-ethylheptanamide (1 g.), m.p. 99–100° (acetone–petroleum ether), lit.[15] m.p. 96°; 2-methyloctanamide (2.21 g.), m.p. 80–81° (acetone–petroleum ether), lit.[16] m.p. 80.8°; and a polar oil (390 mg.).

A mixture of 690 mg. of 4-methyl-2-decanone (490 mg., g.l.c. at 100°) and 4-ethyl-2-nonanone (200 mg., g.l.c.), 2-ethylheptanamide (390 mg.), and 2-methyloctanamide (820 mg.) were isolated from the formamide distillate in the usual manner.

2. **In Sunlight.**—The procedure described A, using 5.6 g. of 2-octene, was followed. The residue (5.4 g.) obtained by the usual work-up was chromatographed on alumina (270 g.) to give a mixture of telomers (160 mg.), 2-ethylheptanamide (1.5 g.), 2-methyloctanamide (2.94 g.), and a polar oil (800 mg.).

Work-up of the recovered formamide distillate led to a residue (2.24 g.) which was chromatographed on alumina (120 g.) to yield 690 mg. of a mixture of 4-methyl-2-decanone (440 mg., g.l.c.) and 4-ethyl-2-nonanone (250 mg., g.l.c.), 2-ethylheptanamide (610 mg.), and 2-methyloctanamide (940 mg.).

E. *cis*-2-Butene and Formamide in Sunlight.—A mixture of *cis*-2-butene (2.82 g., 4.4 ml. as liquid), formamide (40 g.), *t*-butyl alcohol (45 ml.), and acetone (7 ml.) was left in direct sunlight in a Pyrex sealed tube for 50 days. The usual work-up gave a residue (1.6 g.) which was chromatographed on alumina (80 g.). Acetone–petroleum ether (3:17) eluted 600 mg. of 2-methylbutyramide, m.p. 111–112° (acetone–petroleum ether), lit.[17] m.p. 111.7°. An additional 2.2 g. of 2-methylbutyramide was obtained in the usual manner from the recovered formamide distillate.

F. *trans*-2-Butene and Formamide in Sunlight.—The procedure described under E using *trans*-2-butene was followed and led to 2.83 g. of 2-methylbutyramide.

G. Cyclohexene and Formamide. 1. With Ultraviolet Light.—Cyclohexene (4.1 g.) was used for the reaction and the general procedure was followed. The residue obtained by the usual work-up was treated with hot acetone to give 2.1 g. of cyclohexanecarboxamide, m.p. 176–182°. Crystallization from acetone–petroleum ether gave a pure sample, m.p. 184–185°, lit.[18] m.p. 184–185°. Evaporation of the solvent left a residue (2.7 g.) which was chromatographed on alumina (140 g.). Elution with acetone–petroleum ether (1:19) led to an oil (200 mg.) believed to be a mixture of telomers. Acetone–petroleum ether (1:1) further eluted an oil which deposited a solid, m.p. 128–137°. Thin layer chromatography showed it to consist of two compounds having the same R_f values as authentic *cis*- and *trans*-bicyclohexyl-2-carboxamide. The same solvent mixture further eluted 1.42 g. of cyclohexanecarboxamide. Ethanol–acetone (3:7) eluted a polar oil (750 mg.).

Cyclohexylacetone (150 mg.), an unidentified oil (150 mg.), and cyclohexanecarboxamide (600 mg.) were obtained from the formamide distillate in the usual manner. The n.m.r. spectra of all fractions were studied; no signals of vinyl protons could be detected.

2. **In Sunlight.**—The general procedure, using 4.1 g. of cyclohexene, was followed. The usual method of work-up led to 1.7 g. of crude cyclohexanecarboxamide, m.p. 174–182°. Chromatography of the residue (2.76 g.) on alumina (140 g.) yielded a mixture of telomers (300 mg.), cyclohexanecarboxamide (1.77 g.), and a polar oil (610 mg.). Cyclohexylacetone (370 mg.) and cyclohexanecarboxamide (650 mg.) were obtained from the formamide distillate.

H. Methyl Oleate and Formamide. 1. With Ultraviolet Light.—Ten grams of methyl oleate (Fluka, 96%) was used for the reaction. The residue (10.5 g.) obtained by the usual work-up was treated with a mixture of acetone–petroleum ether to give 3.75 g. of a mixture of the carbamoyl esters, m.p. 85–90°. Crystallization from acetone–petroleum ether raised the melting point to 98–100°.

Anal. Calcd. for $C_{20}H_{39}NO_3$: C, 70.33; H, 11.51; N, 4.10. Found: C, 70.61; H, 11.54; N, 4.50.

The solid was shown to consist of a mixture of methyl 9-carbamoyloctadecanoate and methyl 10-carbamoyloctadecanoate by comparison with an authentic mixture (*vide infra*). The isomeric carbamoyl esters could not be separated on chromatography nor did they show any separation in thin layer chromatography; the respective diesters could not be separated in g.l.c.

The residue (7 g.) from the mother liquor was chromatographed on alumina (350 g.). Elution with acetone–petroleum

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[13] 2-Ethylhexanamide and 2-propylpentanamide melt at 101–103° and 123–124°, respectively.

[14] The esters could be separated on columns of squalene at 85° or propylene glycol at 124°.

[15] E. H. Volwiler and D. L. Tabern, *J. Am. Chem. Soc.*, **58**, 1352 (1936).

[16] C. De Hoffmann and E. Barbier, *Bull. soc. chim. Belges*, **45**, 565 (1936).

[17] J. Seib, *Chem. Ber.*, **60**, 1396 (1927).

[18] S. Olsen and E. M. Enkemeyer, *ibid.*, **81**, 359 (1948).

ether (1:49) led to an oil (3.4 g.) which was shown to consist of unreacted starting material. Acetone–petroleum ether (3:17) eluted an oily mixture of telomers (720 mg.). The same solvent mixture further eluted the carbamoyl esters (1.2 g.). Acetone–petroleum ether (3:7) eluted an unidentified oil (580 mg.)

2. **In Sunlight.**—Ten grams of methyl oleate (Fluka, 96%) was used for this experiment. The usual manner of work-up led to 4.5 g. of a mixture of the carbamoyl esters, m.p. 95–98°. Chromatography of the residue (7 g.) from the mother liquor on alumina (350 g.) led to 2.29 g. of unreacted starting material, a mixture of telomers (700 mg.), the carbamoyl esters (2.3 g.), and a polar oil (900 mg.). Somewhat lower yields of the carbamoyl esters were obtained when methyl oleate of technical grade was used. Technical batches of methyl oleate contained impurities which were recovered unchanged from the photochemical reactions.

I. **Oleamide and Formamide in Sunlight.**—A mixture of oleamide (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 on the third day.) After 5 days, a solution of oleamide (3.5 g.), *t*-butyl alcohol (15 ml.), and acetone (2 ml.), was added in five equal portions at 5-day intervals, and the mixture was left in sunlight for another 2 weeks. The precipitate was crystallized from ethanol to yield 1.25 g. of 9-carbamoyloctadecanamide, m.p. 160–163°. Recrystallization gave a pure sample, m.p. 166–167° (ethanol).

Anal. Calcd. for $C_{19}H_{38}N_2O_2$: C, 69.89; H, 11.73; N, 8.58. Found: C, 69.73; H, 11.50; N, 8.47.

Formamide was removed from the filtrate in the usual manner. The residue was treated with saturated aqueous sodium chloride solution and extracted with chloroform. Removal of the solvent left a residue (4.8 g.) which was chromatographed on alumina (250 g.). Elution with acetone–petroleum ether (1:4) led to 1 g. of a solid whose infrared spectrum showed both a ketonic and a carbamoyl function. Ethanol–acetone (1:9) eluted a mixture of the diamides (3.4 g.), m.p. 136–144° (acetone–petroleum ether).

Anal. Calcd. for $C_{19}H_{38}N_2O_2$: C, 69.89; H, 11.73; N, 8.58. Found: C, 69.59; H, 11.55; N, 8.90.

Thin layer chromatography (acetone–petroleum ether) showed two spots, one of which corresponded to 9-carbamoyloctadecanamide. The mixture was chromatographed on Kieselgel G and the first fractions eluted with ethanol–acetone (1:19) contained 10-carbamoyloctadecanamide, m.p. 156–157° (acetone–petroleum ether).

Anal. Calcd. for $C_{19}H_{38}N_2O_2$: C, 69.89; H, 11.73; N, 8.58. Found: C, 70.03; H, 11.59; N, 8.88.

The other fractions consisted of mixture of the two diamides. Further attempts to separate the mixture were unsuccessful.

9-Carbamoyloctadecanoic Acid.—9-Carbamoyloctadecanamide was heated under reflux (nitrogen) over night with a 10% ethanolic potassium hydroxide solution. The usual work-up led to 9-carbamoyloctadecanoic acid, m.p. 126–128° (acetone–petroleum ether).

Anal. Calcd. for $C_{19}H_{37}NO_3$: C, 69.68; H, 11.39; N, 4.28; neut. equiv., 327. Found: C, 70.00; H, 11.01; N, 4.27; neut. equiv., 318.

10-Carbamoyloctadecanoic Acid.—10-Carbamoyloctadecanamide was hydrolyzed by the same procedure to yield 10-carbamoyloctadecanoic acid, m.p. 121–123° (acetone–petroleum ether).

Anal. Calcd. for $C_{19}H_{37}NO_3$: C, 69.68; H, 11.39; N, 4.28. Found: C, 70.11; H, 11.21; N, 4.00.

The carbamoyl esters were prepared by treatment of the carbamoyl acids with diazomethane. Methyl 9-carbamoyloctadecanoate showed m.p. 108–109° (acetone–petroleum ether).

Anal. Calcd. for $C_{20}H_{39}NO_3$: C, 70.33; H, 11.51; N, 4.1. Found: C, 70.32; H, 11.69; N, 4.11.

Methyl 10-carbamoyloctadecanoate exhibited m.p. 106–108° (acetone–petroleum ether).

Anal. Calcd. for $C_{20}H_{39}NO_3$: C, 70.33; H, 11.51; N, 4.10. Found: C, 70.04; H, 11.12; N, 4.06.

The mixture of the carbamoyl esters showed m.p. 98–100°. Both compounds and their mixture showed the same R_f values in thin layer chromotography as the ones of the carbamoyl esters obtained from the reaction of methyl oleate and formamide.

9-Carboxyoctadecanoic Acid.—A mixture of 9-carbamoyloctadecanamide (0.5 g.), potassium hydroxide (1.5 g.), and ethylene glycol (10 ml.) was heated under reflux (nitrogen) for 3 days until no more ammonia was evolved. The usual work-up led to the crude diacid which was purified through boiling with charcoal in petroleum ether. Pure 9-carboxyoctadecanoic acid showed m.p. 79–81° (petroleum ether).

Anal. Calcd. for $C_{19}H_{36}O_4$: C, 69.47; H, 11.05. Found: C, 69.16; H, 10.90.

10-Carboxyoctadecanoic Acid.—The procedure described above was followed using 10-carbamoyloctadecanamide and led to 10-carboxyoctadecanoic acid, m.p. 66–68° (petroleum ether).

Anal. Calcd. for $C_{19}H_{36}O_4$: C, 69.47; H, 11.05. Found: C, 69.45; H, 11.03.

Authentic 9-Carboxyoctadecanoic Acid.—Nonyl diethyl malonate (3.72 g., 0.13 mole) was added to a solution of sodium (3 g., 0.13 g.-atom) in dry *n*-butyl alcohol (50 ml.), followed by the addition of ethyl ω-bromooctoate[19] (40 g.). The mixture was heated under reflux for 48 hr. The usual work-up led to an oil which was distilled *in vacuo* and the fraction, b.p. 150–220° (0.3 mm.) (50.5 g.), was collected. Hydrolysis of 25 g. of the distillate was accomplished with 50% ethanolic potassium hydroxide solution in the usual manner and the resulting triacid was decarboxylated at 180°. The residue was boiled with charcoal in petroleum ether to yield 11.2 g. (63%) of 9-carboxyoctadecanoic acid, m.p. 66–72°. Crystallization from petroleum ether gave a pure sample, m.p. 80–82°.

Anal. Calcd. for $C_{19}H_{36}O_4$: C, 69.47; H, 11.05; neut. equiv., 164. Found: C, 69.38; H, 10.91; neut. equiv., 159.

Authentic 10-Carboxyoctadecanoic Acid.—The above procedure using octyl diethyl malonate and ethyl ω-bromononanoate was followed leading to crude 10-carboxyoctadecanoic acid (10.6 g.), m.p. 62–67°. Crystallization from petroleum ether gave a pure sample, m.p. 66–67°.

Anal. Calcd. for $C_{19}H_{36}O_4$: C, 69.47; H, 11.05; neut. equiv., 164. Found: C, 69.40; H, 10.98; neut. equiv., 169.

The diamides of the authentic diacids were prepared through the diacid chlorides and ammonia and showed m.p. and m.m.p. 166–167° and 155–156°, respectively.

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(19) Prepared from azelaic acid monoethyl ester by the method of H. Hunsdiecker and C. Hunsdiecker, *Chem. Ber.*, **75**, 291 (1942).