THE LIGHT-INDUCED ADDITION OF 2-PYRROLIDONE TO OLEFINS

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Abstract—The acetone-initiated photochemical addition of 2-pyrrolidone to olefins is described. The reaction leads to two of the possible isomeric 1:1-adducts, the 3-alkyl-2-pyrrolidones (one part) and the 5-alkyl-2-pyrrolidones (2 parts) in yields of up to 60 %. A proposed mechanism for the reaction is discussed.

INTRODUCTION

THE photolysis of amides has been reported to yield a variety of products derived from decomposition of the amide molecule to small fragments. Thus, the photolysis of acetamide with short UV light ($\lambda < 260$ nm) led to methane, ammonia and aceto-nitrile, besides other decomposition products. The photolysis of propionamide and higher homologous amides led similarly to decomposition products resulting from cleavage of C—C and C—N bonds in the photolyzed molecules.[2] The intermediates formed in these photolysis reactions might be usefully scavenged by olefins and so provide a useful route to derivatives of amides.[3]

An attempted scavenging with terminal olefins of intermediates produced by direct photolysis of lactams led to traces only of addition products possessing a lactam skeleton.[4] It could, however, be expected that more specific irradiation conditions (such as use of photosensitizers or photoinitiators) might lead to products having this skeleton. Similar reactions have been shown to produce intermediates (free radicals) of the substrates involved, which could subsequently be scavenged by a variety of olefins.[5]

The present study was undertaken with the aim of investigating the interaction of excited ketone molecules with lactams and the possible exploitation of the chemical species produced for synthetic purposes. It was expected that scavenging of these species would lead to the formation of substituted lactams by a simplified route.

RESULTS

It has been found that irradiation of 2-pyrrolidone in the presence of acetone and terminal olefin leads to the addition of 2-pyrrolidone to the olefin to give two of the possible isomeric alkyl-2-pyrrolidones resulting from addition to the terminal carbon of the double bond (anti-Markovnikov). Mixtures of 3- and 5-alkyl-substituted-2-pyrrolidones (1:1-adducts) are obtained as the major products of the reaction. A preliminary communication concerning these reactions has been reported,[4] and the present publication includes full details of the reaction, its application to a variety of terminal olefins and to cyclohexene, and a full description of the by-products

obtained. The reactions can be formulated as follows,

$$R = Et; Bu; C_5H_{11}; C_6H_{13}; C_8H_{17}; H_3COOC(CH_2)_2—$$
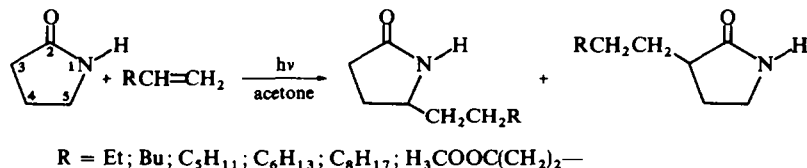
In all cases studied the C_5-alkyl isomer predominated in the mixture of 1:1 adducts, usually in the ratio of 2:1. The reactions studied and the major 1:1-adducts isolated are summarized in Table 1.

TABLE 1. ADDITION PRODUCTS OF 2-PYRROLIDONE AND OLEFINS
(Initiated by Acetone)

Olefin[a]	Product (1:1-adduct)	Yields (%)[b]	Source of Light
1-Hexene	3-Hexyl-2-Pyrrolidone	13	Ultraviolet[c]
	5-Hexyl-2-Pyrrolidone	27	
	3-Hexyl-2-Pyrrolidone	20	Sun
	5-Hexyl-2-Pyrrolidone	38	
1-Heptene	3-Heptyl-2-Pyrrolidone	13	Ultraviolet[d]
	5-Heptyl-2-Pyrrolidone	27	
	3-Heptyl-2-Pyrrolidone	17	Sun
	5-Heptyl-2-Pyrrolidone	33	
1-Octene	3-Octyl-2-Pyrrolidone	12	Ultraviolet[e]
	5-Octyl-2-Pyrrolidone	27	
	3-Octyl-2-Pyrrolidone	20	Sun
	5-Octyl-2-Pyrrolidone	36	
	3-Octyl-2-Pyrrolidone	23	Ultraviolet[d,f]
	5-Octyl-2-Pyrrolidone		
1-Decene	3-Decyl-2-Pyrrolidone	12	Ultraviolet[d]
	5-Decyl-2-Pyrrolidone	27	
	3-Decyl-2-Pyrrolidone	17	Sun
	5-Decyl-2-Pyrrolidone	38	
Cyclohexene	3-Cyclohexyl-2-Pyrrolidone	45	Sun
	5-Cyclohexyl-2-Pyrrolidone		
Ethyl 4-Pentenoate	Ethyl 5-(2-Pyrrolidonyl-3)-pentanoate	14	Sun
	Ethyl 5-(2-pyrrolidonyl-5)-pentanoate	34	

[a] The mole ratio of 2-pyrrolidone:olefin was 20:1.
[b] Based on the olefin employed.
[c] Hanovia 200 W high pressure mercury lamp with a Pyrex filter.
[d] Hanau Q81 with a Pyrex filter.
[e] With a quartz filter.
[f] With Benzophenone.

The isomeric 3-alkyl- and 5-alkyl-2-pyrrolidones were separated by chromatography on silica gel. The first fractions included the 3-alkyl isomer, while the last ones consisted of the 5-alkyl isomer. The compositions of intermediate fractions, which contained both isomers, were determined by GLC on an Apiezon L column. Both

types of the 1 : 1 adducts, i.e. the 3-alkyl and the 5-alkyl-2-pyrrolidones, were character-
ized by their physical properties, elemental analyses, IR, NMR and mass spectra,
and in some cases they were further compared with authentic samples. The latter were
prepared from the appropriate alkyl-γ-butyrolactones and ammonia.[6, 7] All pairs
of isomeric 1:1 adducts showed characteristic absorption in the NMR spectrum in
the τ 6·4 and 7·8 regions (—CHR—NH—CO— and —NH—COCHR—, respectively),
which assisted in determining their structures. With cyclohexene, addition products
were obtained rather than products from allylic substitution. The 5-alkyl isomer
could be separated from the 1:1 adduct mixture.

Telomeric products, resulting from addition of 2-pyrrolidone to more than one
molecule of the olefin, were also isolated, though in small quantities. These were
characterized through elemental analyses, NMR and mass spectra. In addition, a
sparingly soluble product has been obtained, whose elemental analysis, IR and NMR
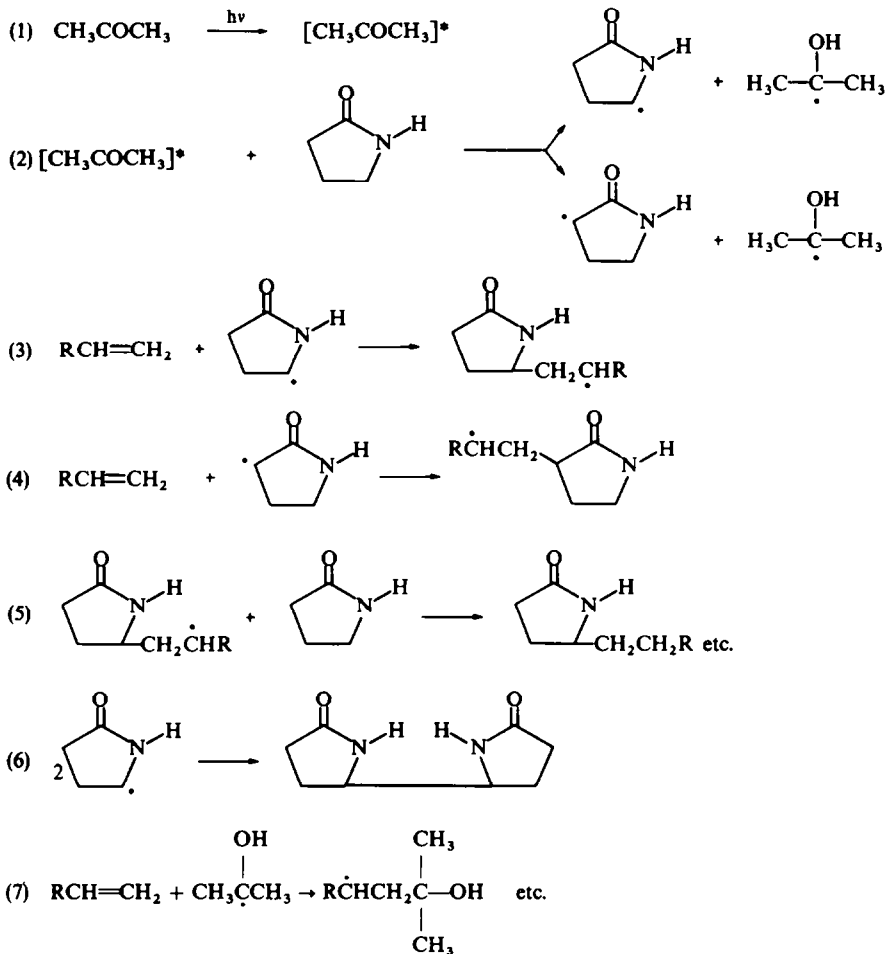spectra suggest the dehydrodimer structure
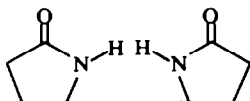
Addition products of the photoinitiator moiety and the olefins, such as 2-methyl-2-
alkanols and alkyl methyl ketones were also obtained and identified by standard
procedures.[8]

DISCUSSION

Photoalkylation reactions reported previously[5] showed that these reactions can
be induced directly by light or initiated photochemically by ketones with higher
yields of the reaction products. The direct light-induced reactions were initiated with
light of short wavelength (quartz filtered), whereas in the ketone-initiated ones light
of relatively long wavelengths (Pyrex filtered; $\lambda > 290$ nm) was employed. A similar
photochemical ketone-initiated reaction of 2-pyrrolidone and terminal olefins was
shown to give high yields of the 1:1 addition products, whereas the direct light-
induced reaction failed to yield any appreciable amounts of adducts of this type.
Thus, the presence of the ketonic compound seems to be vital for the photoaddition
of 2-pyrrolidone to terminal olefins. The ketone molecule serves as the light absorbing
agent in these reactions where light of wavelengths $\lambda > 290$ nm is employed, the
other reactants absorbing light of much shorter wavelengths. The interaction of the
photoactivated ketone molecule with 2-pyrrolidone results in the abstraction of a
hydrogen atom from the latter to produce 2-pyrrolidonyl free radicals which react
further. It has been shown that a carbonyl or an amino function facilitate the forma-
tion of free radicals in the respective alpha positions in photochemical as well as in
free radical reactions.[9-11] The 2-pyrrolidone molecule possesses both types of these
functional groups, and hence this molecule has two potentially reactive sites for the
H atom abstraction process, namely C_3 and C_5. The two respective 2-pyrrolidonyl
free radicals are generated through the process of H atom abstraction by the photo-
activated ketone molecule. This is evidenced by the formation of the corresponding
alkyl-2-pyrrolidones in the presence of olefins. These products result from scavenging

of both types of free radicals by the olefins. Thus, the reaction can be summarized as follows

(1) CH_3COCH_3 $\xrightarrow{h\nu}$ $[CH_3COCH_3]^*$ → (2-pyrrolidone radical, N–H) + $H_3C{-}\underset{\cdot}{\overset{OH}{C}}{-}CH_3$

(2) $[CH_3COCH_3]^*$ + (2-pyrrolidone, N–H) → (2-pyrrolidone radical, N–H) + $H_3C{-}\underset{\cdot}{\overset{OH}{C}}{-}CH_3$

(3) $RCH{=}CH_2$ + (2-pyrrolidone radical, N–H) → (2-pyrrolidone, N–H)$-CH_2\dot{C}HR$

(4) $RCH{=}CH_2$ + $\cdot$(2-pyrrolidone radical, N–H) → $R\dot{C}HCH_2{-}$(2-pyrrolidone, N–H)

(5) (2-pyrrolidone, N–H)$-CH_2\dot{C}HR$ + (2-pyrrolidone radical, N–H) → (2-pyrrolidone, N–H)$-CH_2CH_2R$ etc.

(6) 2 (2-pyrrolidone radical, N–H) → (dehydrodimer: two pyrrolidone rings joined)

(7) $RCH{=}CH_2 + CH_3\dot{C}CH_3 \rightarrow R\dot{C}HCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OH$ etc.

Experimental evidence for a mechanism involving an H atom abstraction process from the lactam by the excited ketone molecule is supported by the formation of isopropanol and 2-methyl-2-alkanols in the reaction mixture. These are derived from a ketyl radical which results from the H atom abstraction process.[12, 13] The free radical nature of the subsequent steps, i.e. the addition of the 2-pyrrolidone moieties to the olefins, is proved by the formation of 1:1 addition products of the anti-Markovnikov type, telomers and dehydrodimers of 2-pyrrolidone. The formation of alkyl methyl ketones, which result from the addition of an acetonyl free radical $\dot{C}H_2COCH_3$ to the olefins is also in accordance with the proposed free radical mechanism. The ratio of approximately 1:2 between the 3-alkyl- and 5-alkyl-2-pyrrolidones formed, i.e. the predominance of the alkylation at the carbon alpha to the N atom, is a general feature in all the reactions studied. Similar results were obtained in the peroxide-induced reactions of 2-pyrrolidone and olefins at elevated

temperatures.[7] The photochemical reaction of N-methylacetamide and olefins also leads to a mixture of both types of 1:1 addition products, where the one resulting from alkylation at the carbon attached to the N atom predominates.[14,†] It is noteworthy that in the similar photoalkylation reaction of γ-butyrolactone or tetrahydro-γ-pyrone with olefins, alkylation takes place almost exclusively at the C atom alpha to the carbonyl function.[15,16]

EXPERIMENTAL

B.ps and m.ps are uncorrected. Silica gel (Kieselgel 0·05–0·02 mm, Merck, Darmstadt) and Merck "Acid Washed" alumina were used for chromatography unless otherwise stated. GLC was carried out on an Aerograph A 90 P on a 20 feet × ⅜ inch column. Columns of 0·2% Apiezon L on glass beads were used for the 2-pyrrolidone derivatives, and Carbowax 400 for the isopropanol, acetone and olefins, at the temp stated. The NMR spectra were determined on a Varian A-60 spectrophotometer in $CDCl_3$ with TMS as an internal reference. The chemical shifts are given in τ values. Analyses were carried out in our microanalytical section directed by Mr. R. Heller.

Experiments with UV light were conducted in an immersion apparatus using Hanau Q81 and Hanovia 200 W high press Hg vapour lamps, which were cooled internally with running water. Pyrex filters were used for all experiments unless otherwise stated. Agitation was achieved by magnetic stirring. N_2 was bubbled through the reaction mixture for the first 15 min. Reactions in sunlight were performed in Pyrex tubes. Typical experiments are described for 1-hexene. Other experiments were carried out under similar conditions unless otherwise stated.

Reagents. 2-Pyrrolidone was freshly distilled before use; acetone (Fluka, absolute) and benzophenone (Fluka) were used without purification. The olefins were shaken with 2% $FeSO_4$ aq, dried (Na_2SO_4), and before use were freshly distilled and filtered through a short column of "Alcoa" activated alumina F 20. Authentic alkyl-2-pyrrolidones employed were prepared by reacting the corresponding alkyl-γ-butyrolactones and ammonia at 250–300°.[6,7]

2-Pyrrolidone and 1-hexene

(1) *With UV light (Hanovia 200 W)*. A mixture of 2-pyrrolidone (175 g), acetone (5 ml) and 1-hexene (0·5 g) was irradiated for 1 hr. A soln of 1-hexene (8·1 g) in acetone (20 ml) was then added in 8 equal portions at 1 hr intervals. The mixture was irradiated until complete consumption of the olefin (ca. 30 hr, checked by GLC at 60°). Excess reagents were distilled under reduced press on a steam bath and the distillate was shown to contain acetone and isopropanol (0·1 g; GLC at 100°); the latter was characterized as the 3,5-dinitrobenzoate, m.p. and mixed m.p. 121–122°. One quarter of the residue was chromatographed on silica gel (2000 g). Elution with acetone–pet. ether (1:19) gave an oil (0·2 g) believed to be a mixture of telomers. The same solvent mixture further eluted 2-methyl-2-octanol (0·4 g), which was characterized by its retention time in GLC (120°), IR spectrum and 3,5-dinitrobenzoate, m.p. and mixed m.p. 53–54°. 2-Nonanone (0·01 g) was eluted next and was characterized by GLC, IR spectrum and as the 2,4-dinitrophenylhydrazone which had m.p. and mixed m.p. 48–49° (EtOH). [Lit.[17] m.p. 48–49°]. The same solvent mixture (1:9) eluted a 2:1 telomer fraction (0·13 g). (Found: C, 75·99; H, 12·42; N, 5·48. $C_{16}H_{31}NO$ requires: C, 75·83; H, 12·33; N, 5·53%). Acetone–pet. ether (3:7) eluted a mixture of 3-hexyl-2-pyrrolidone and 5-hexyl-2-pyrrolidone (1·63 g).

Further elution with the same solvent mixture (4:6) gave unchanged 2-pyrrolidone (40 g). EtOH–acetone (1:9) mixture eluted a solid (0·25 g), m.p. 250–280° (dec). (Found: C, 57·28; H, 7·35; N, 15·93; $C_8H_{12}N_2O_2$ requires: C, 57·13; H, 7·19; N, 16·66%); v_{max} (KBr) 1680 cm^{-1}; NMR (trifluoroacetic acid): a signal at τ 1·65 (2H; —N<u>H</u>—) and multiplets centered at 5·7 (2H; —NH—C<u>H</u>—C<u>H</u>—NH—) and 7·5 (8H; ring —C<u>H</u>$_2$—C<u>H</u>$_2$—CO—). The same solvent mixture (1:4) eluted a glassy oil (0·45 g). (Found: C, 58·33; H, 8·63; N, 11·03%).

The mixture of hexylpyrrolidones (1·63 g) obtained above was separated chromatographically on Kieselgel H (Merck, Darmstadt) (50 g) in acetone–pet. ether (1:4) to yield fractions of pure 3-hexyl-2-pyrrolidone, m.p. 65–66° (acetone–pet. ether). (Found: C, 70·49; H, 11·06; N, 8·11. $C_{10}H_{19}NO$ requires: C, 70·96; H, 11·32; N, 8·28%). The compound was found to be identical with an authentic sample. NMR:

† Friedman and Shechtes as well as Nikishin and Mustafaev have reported that the peroxide-induced reactions of N-substituted acetamides and olefins led to alkylation at the carbon attached to nitrogen.

a broad signal at τ 3·7 (1H; —NH—), multiplets centered at 6·6 (2H; —CH$_2$—CH$_2$—NH—) and 7·8 (3H; ring —CH$_2$—CH—CO—), a signal at 8·7 (10H; —(CH$_2$)$_5$—CH$_3$), and a triplet at 9·1 (3H; —CH$_2$CH$_3$). Later fractions were eluted which contained mixtures of the two isomers, the amounts of which were determined by GLC (250°). The last fractions to be eluted gave pure 5-hexyl-2-pyrrolidone, m.p. 48–49° (acetone–pet. ether). (Found: C, 70·51; H, 11·10; N, 8·14. C$_{10}$H$_{19}$NO requires: C, 70·96; H, 11·32; N, 8·28%); NMR: a signal at τ 2·4 (1H; —NH—), multiplets centered at 6·4 (1H; —CHRNH) and 7·7 (4H; ring —CH$_2$—CH$_2$—CO—), a signal at 8·7 (10H; —(CH$_2$)$_5$—CH$_3$), and a triplet (3H; —(CH$_2$)$_5$—CH$_3$). The ratios of the two isomers were determined by GLC (250°) and showed that the mixture consisted of 3-hexyl-2-pyrrolidone (0·54 g) and 5-hexyl-2-pyrrolidone (1·08 g). The chromatographic separation between the two isomers in the various experiments varied with the amounts employed and the number of fractions taken during the chromatography.

A total of 3-hexyl-2-pyrrolidone (2·17 g; 13%) and 5-hexyl-2-pyrrolidone (4·35 g; 27%) were obtained from the experiments described. An alternative procedure for working up the reaction mixture involved removal of unreacted 2-pyrrolidone at 90–95°/1 mm and distillation of the mixture of the 1:1 adducts at 110–145°/0·3 mm. The mixture of 3-hexyl-2-pyrrolidone and 5-hexyl-2-pyrrolidone was then chromatographed to yield pure samples of the isomers as described.

(2) *In sunlight.* A mixture of 2-pyrrolidone (84·5 g), acetone (5 ml) and 1-hexene (0·5 g) was exposed to direct sunlight for 1 day. A soln of 1-hexene (3·7 g) in acetone (5 ml) was then added in 8 equal portions at one-day intervals, and the mixture was left in direct sunlight for another 14 days until complete consumption of the olefin. The reaction mixture was worked up according to the procedure described above and led to unchanged acetone and isopropanol (0·07 g) in the volatile fraction. The residue was chromatographed on silica gel to afford a mixture of telomers (0·14 g), 2-methyl-2-octanol (1·43 g), 2-nonanone (0·05 g), a 2:1 telomer (0·5 g), a mixture (4·9 g; 58%) of 3-hexyl-2-pyrrolidone (1·7 g; 20%) and 5-hexyl-2-pyrrolidone (3·2 g; 38%) which was worked up as above. Further were eluted unchanged pyrrolidone (81 g), a dehydro-dimer fraction (0·47 g), and polar oils (1·25 g).

2-Pyrrolidone and 1-heptene

(1) *With UV light* (Q81). The procedure described for 1-hexene was followed using 2-pyrrolidone (106 g), 1-heptene (4·9 g) and acetone (10 ml). Excess reagents were removed under reduced press and the fraction b.p. 135–145°/0·15 mm (4·9 g) was chromatographed on alumina. The usual method of work-up as described above led to a mixture of heptyl-2-pyrrolidones (3·7 g). (Found: C, 72·04; H, 11·43; N, 7·86. C$_{11}$H$_{21}$NO requires: C, 72·08; H, 11·55; N, 7·64%). This fraction contained 3-heptyl-2-pyrrolidone (1·2 g; 13%), and 5-heptyl-2-pyrrolidone (2·5 g; 27%). 3-Heptyl-2-pyrrolidone had m.p. 56–57° (acetone–pet. ether). (Found: C, 72·02; H, 11·52. C$_{11}$H$_{21}$NO requires: C, 72·08; H, 11·55%); NMR: a signal at τ 2·7 (1H; —NH—), multiplets at 6·25 (2H; —CH$_2$—NH—) and 7·75 (3H; ring —CH$_2$—CH—CO—), a signal at 8·7 (12H; —(CH$_2$)$_6$—CH$_3$), and a triplet at 9·1 (3H; —(CH$_2$)$_6$CH$_3$). The compound was identical with an authentic sample. 5-Heptyl-2-pyrrolidone showed m.p. 46–47° (acetone–pet. ether). (Found: C, 72·54; H, 11·42. C$_{11}$H$_{21}$NO requires: C, 72·08; H, 11·55%); NMR: A signal at τ 2·2 (1H; NH—), multiplets at 6·4 (1H; —CHR—NH—) and 7·7 (4H; ring —CH$_2$—CH$_2$—CO—), a signal at 8·7 (12H; —(CH$_2$)$_6$—CH$_3$) and a triplet at 9·1 (3H; —(CH$_2$)$_6$CH$_3$).

(2) *In sunlight.* The general procedure for reaction in sunlight was followed employing 2-pyrrolidone (85 g), 1-heptene (4·9 g) and acetone (10 ml). The usual method of work-up led to isopropanol (1·7 g), a mixture of telomers (0·02 g), 2-decanone [0·41 g; GLC at 120°; 2,4-dinitrophenylhydrazone, m.p. and mixed m.p., 73–74° (EtOH) lit.[17] m.p. 73·5–74°)], 2-methyl-2-nonanol [1·15 g; GLC at 120°; 3,5-dinitro-benzoate, m.p. and mixed m.p. 58–60° (lit.[8] 58–60)], 3-heptyl-2-pyrrolidone (1·6 g; 17%), 5-heptyl-2-pyrrolidone (3 g; 33%), unchanged 2-pyrrolidone, a dehydrodimer fraction (0·3 g) and polar oils (1·1 g).

2-Pyrrolidone and 1-octene

(1) *With UV light* (Q81; *quartz filter*). Starting with 1-octene (5·1 g), the usual procedure of work-up gave a fraction (3·6 g), b.p. 160–165°/0·15 mm, which solidified. This was chromatographed on silica gel to yield 3-octyl-2-pyrrolidone (1·1 g; 12·3%), m.p. 80–81° (acetone–pet. ether) [lit.[7] 80–81°]. (Found: C, 72·96; H, 11·63; N, 7·09. Calc. for C$_{12}$H$_{23}$NO: C, 73·04; H, 11·75; N, 7·10%); NMR: a signal at 2·6 (1H; —NH—), multiplets at 6·7 (2H; —CH$_2$—NH—) and 7·7 (3H; ring —CH$_2$—CHR—CO—), a signal at 8·7 (14H; —(CH$_2$)$_7$—CH$_3$) and a triplet at 9·1 (3H; —(CH$_2$)$_7$—CH$_3$). The compound was identical with an authentic sample. Further elution gave 5-octyl-2-pyrrolidone (2·4 g; 26·8%), m.p. 60–61° (acetone–pet. ether). [lit.[7] m.p. 56–57·5°]. (Found: C, 73·35; H, 11·50; N, 6·94. Calc. for C$_{12}$H$_{23}$NO: C, 73·04; H,

11·75; N, 7·10%); NMR: a signal at τ 2·6 (1H; —NH—), multiplets at 6·4 (1H; —CHR—NH—) and 7·7 (4H; ring —CH$_2$—CH$_2$—CO—), a signal at 8·7 (14H; —(CH$_2$)$_7$—CH$_3$), and a triplet at 9·1 (3H; —(CH$_2$)$_7$—CH$_3$).

(2) *In sunlight.* Starting with 1-octene (5·6 g), the usual work-up led to isopropanol, 2-undecanone [0·07 g; GLC at 120°; 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 63–64° (lit.[17] 64·5–65°)], 2-methyl-2-decanol [GLC at 120°; 3,5-dinitrobenzoate, m.p. and mixed m.p. 47–48° (lit.[8] 47–48°)], a mixture of telomers, 3-octyl-2-pyrrolidone (1·95 g; 20%), 5-octyl-2-pyrrolidone (3·6 g; 36%), unreacted pyrrolidone, a dehydrodimer fraction (0·5 g) and glassy polar oils (1·4 g). (Found: C, 58·33; H, 8·57; N, 11·03%).

A similar experiment using benzophenone (5 g) instead of acetone led to a mixture of 3-octyl- and 5-octyl-2-pyrrolidone (2·3 g; 23%).

2-*Pyrrolidone and* 1-*decene.*

(1) *With UV light* (Q81). The general procedure was followed using 2-pyrrolidone (116 g), 1-decene (7 g) and acetone (15 ml). The usual work-up and distillation led to a solid fraction (4·7 g), b.p. 140–160°/0·1 mm, which was chromatographed on silica gel to give 3-decyl-2-pyrrolidone (1·3 g; 12%), m.p. 85–86° (acetone–pet. ether). (Found: C, 74·47; H, 11·97; N, 6·51. C$_{14}$H$_{27}$NO requires: C, 74·61; H, 12·08; N, 6·22%). The compound was identical with an authentic sample. The 5-decyl-2-pyrrolidone (3 g; 27%) had m.p. 65–66° (acetone–pet. ether),. (Found: C, 74·48; H, 11·92; N, 6·44. C$_{14}$H$_{27}$NO requires: C, 74·61; H, 12·08; N, 6·22%); NMR: a signal at τ 2·85 (1H; —NH—), multiplets at 6·4 (1H; —CHR—NH—) and 7·7 (4H; ring —CH$_2$—CH$_2$—CO—), a signal at 8·7 [18H; —(CH$_2$)$_9$—CH$_3$], and a triplet at 9·1 [3H; —(CH$_2$)$_7$—CH$_3$].

(2) *In sunlight.* Starting with 1-decene (7 g), the usual work-up led to isopropanol, 2-tridecanone [GLC at 120°; 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 69–70° (lit.[17] 70–71°)], 2-methyl-2-dodecanol (GLC at 120°), 3-decyl-2-pyrrolidone (1·9 g; 17%) and 5-decyl-2-pyrrolidone (4·9 g; 38%), a dehydrodimer fraction (0·32 g) and glassy oils (1·4 g). (Found: C, 58·17; H, 8·68; N, 11·07%).

2-*Pyrrolidone and ethyl-4-pentenoate in sunlight*

The general procedure for reactions in sunlight was followed employing ethyl-4-pentenoate (6·4 g). The usual method of work-up gave ethyl 5-(2-pyrrolidonyl-3)-pentanoate (1·45 g; 14%), m.p. 56–57° (acetone–pet. ether). (Found: C, 61·97; H, 9·14; N, 6·71; C$_{11}$H$_{19}$NO$_3$ requires: C, 61·94; H, 8·98; N, 6·57%); v_{max} (KBr) 1685, 1720 cm^{-1}. NMR: a signal at 2·6 (1H; —NH—), a quartet at 5·85 (2H; —O—CH$_2$—CH$_3$), multiplets at 6·7 (2H; —CH$_2$—NH—) and 7·7 (3H; ring —CH$_2$—CHR—CO—), a multiplet at 8·4 [8H; —(CH$_2$)$_4$—COOEt] superimposed on a triplet centered at 8·75 (3H; —COOCH$_2$CH$_3$).

Ethyl 5-(—2 pyrrolidonyl-5)-pentanoate (3·62 g; 34%) was eluted as an oil, n_D^{19} 1·4762. (Found: C, 60·71; H, 9·02; N, 6·31. C$_{11}$H$_{19}$NO$_3$ requires: C, 61·94; H, 8·98; N, 6·57%); v_{max} (Neat) 1685, 1720 cm^{-1}. NMR: a signal at 2·8 (1H; —NH—), a quartet at 5·9 (2H; —O—CH$_2$—CH$_3$) multiplets at 6·3 (1H; —CHR—NH—) and 7·7 (4H; ring —CH$_2$—CH$_2$—CO—), a multiplet at 8·5 (8H; —(CH$_2$)$_4$—COOEt) superimposed on a triplet centered at 8·8 (3H; —COOCH$_2$CH$_3$).

2-*Pyrrolidone and cyclohexene in sunlight*

Starting with cyclohexene (4·1 g), the usual work-up followed by chromatography on silica gel, led to a solid fraction (3·8 g; 45%), m.p. 87–92° (acetone–pet. ether). (Found: C, 71·41; H, 9·89; N, 8·62. C$_{10}$H$_{17}$NO requires: C, 71·81; H, 10·25; N, 8·38%); mass spectrum: molecular peak of m/e 167 (C$_{10}$H$_{17}$NO requires: 167). Rechromatography led to a pure sample of 5-cyclohexyl-2-pyrrolidone, m.p. 117–118° (acetone–pet. ether). (Found: C, 71·72; H, 10·37; N, 8·31, C$_{10}$H$_{17}$NO requires: C, 71·81; H, 10·25; N, 8·38%); NMR: a signal at 2·7 (1H; —NH—), multiplets at 6·6 (1H; —CHR—NH), a multiplet at 7·7 and signals at 8·2 and 8·9 (together 15H; cyclohexyl methylenes and methine and —CH—CH$_2$—CO—).

2-*Pyrrolidone and* 1-*butene in sunlight*

A mixture of 2-pyrrolidone (85 g), acetone (10 ml) and 1-butene (about 5 ml) was exposed in a sealed Pyrex tube to direct sunlight for 2 weeks. The residue obtained by the usual work-up was chromatographed to give an oily mixture of 3-butyl- and 5-butyl-2-pyrrolidone. (Found: C, 68·21; H, 10·82; N, 9·40. C$_8$H$_{15}$NO requires: C, 68·04; H, 10·71; N, 9·92%; mass spectrum: molecular peak of m/e 141. (C$_8$H$_{15}$NO requires: 141).

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