## Journal of Macromolecular Science, Part A

## N,N'-Divinylureas: Further Polymerization Studies and Spectroscopic Investigation of Structure

G. C. Corfield[a]; A. Crawshaw[a]; H. H. Monks[a]

[a] Department of Chemistry and Biology, Sheffield Polytechnic, Sheffield, England

## PLEASE SCROLL DOWN FOR ARTICLE

# N,N'-Divinylureas: Further Polymerization Studies and Spectroscopic Investigation of Structure

G. C. CORFIELD, A. CRAWSHAW, and H. H. MONKS

Department of Chemistry and Biology
Sheffield Polytechnic
Sheffield S1 1WB, England

## ABSTRACT

Homopolymerization of 1, 3-divinylimidazolid-2-one and 1, 3-divinylhexahydropyrimid-2-one produces cross-linked polymers. 1, 3-Diphenyl-1, 3-divinylurea (DPDVU) and 1, 3-dimethyl-1, 3-divinylurea (DMDVU) could not be polymerized. 1-Ethyl-3-vinylimidazolid-2-one yields a soluble linear polymer. All of the N, N'-divinylureas have a strong absorption band in the UV region of the spectrum, which is good evidence for conjugation of the electron pairs on the nitrogen atom with the $\pi$-electrons of the vinyl and carbonyl double bond. Further support for conjugation is obtained from NMR and IR spectroscopy. Such conjugation would tend to favor intermolecular propagation rather than the cyclopolymerization mechanism. The inability of DPDVU to polymerize is explained by the fact that addition of a radical to this monomer produces a resonance stabilized free radical. The failure of

the <u>inter</u>molecular propagation reaction with DMDVU is
attributed to steric hinderance. Rapid hydrolysis of the
N-vinyl group in these compounds takes place in aqueous
solution, yielding acetaldehyde and the corresponding urea.

## INTRODUCTION

N, N'-Divinylureas (I) are examples of 1, 6-dienes, and as such
might be expected to yield linear polymers by the cyclopolymerization
mechanism [1] under suitable conditions. However, the results re-
ported for polymerizations of these monomers [2-6] indicate that

$$CH_2 = CH\underset{R}{N} \longrightarrow \overset{\overset{O}{\|}}{C} \longrightarrow \underset{R}{N}CH = CH_2$$
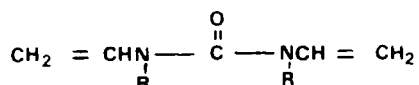
(1)

cyclopolymers are not formed. In an attempt to offer some explana-
tion for the noncyclopolymerization of N, N'-disubstituted-N, N'-
divinylureas, Crawshaw and Jones [6] proposed for their structure
a coplanar situation produced by conjugation of the lone pair electrons
on the nitrogen atoms with the carbonyl and vinyl double bonds (II).
Such a planar arrangement would tend to favor intermolecular propa-
gation and the cross-linked polymers obtained experimentally, rather
than the cyclopolymerization mechanism.

This paper describes further polymerization studies of 1, 3-
divinylimidazolid-2-one (DVI), 1,3-divinylhexahydropyrimid-2-one
(DVHHP), and 1,3-diphenyl-1,3-divinylurea (DPDVU). The synthesis
and polymerization behavior of 1,3-dimethyl-1,3-divinylurea (DMDVU)
and 1-ethyl-3-vinylimidazolid-2-one (EVI, which was synthesized to
assist in the structural investigation of N, N'-divinylureas) are also
described. Investigation of the structures of N, N'-divinylureas by UV,
IR, and NMR spectroscopy was carried out to seek evidence for con-
jugation of the electron pairs on the nitrogen atoms with the $\pi$-electrons
of the vinyl and carbonyl double bonds.

## POLYMERIZATION STUDIES

The polymerization of DVI was achieved using various initiation
techniques, the results and conditions being summarized in Table 1.
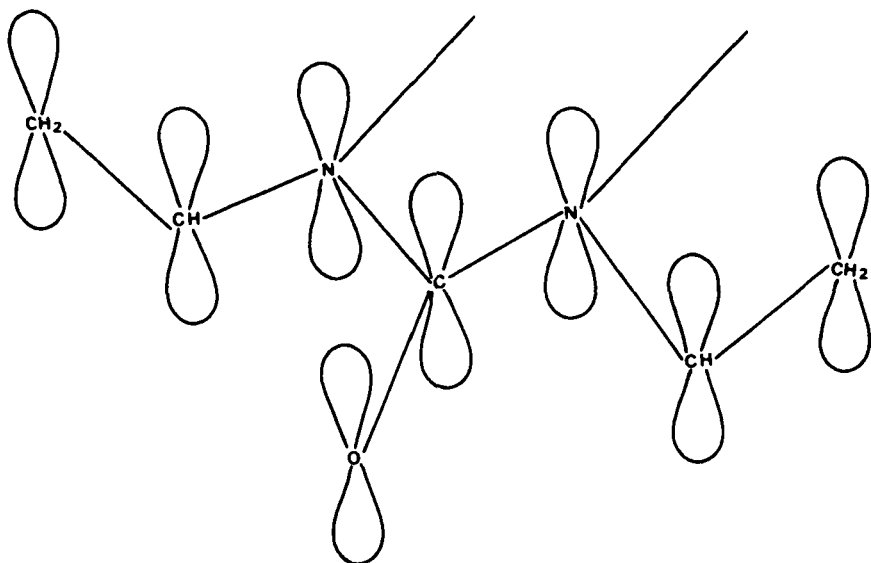
$\overline{11}$

The polymers were isolated either directly from the polymerization reaction, if their insolubility caused spontaneous precipitation, or by dropwise addition into vigorously stirred ether or light petroleum.

The polymers isolated from all polymerizations were insoluble in a wide variety of solvents, infusible, and hence cross-linked. The IR spectra of poly(1,3-divinylimidazolid-2-one) showed residual unsaturation, the spectra being almost identical to those of Jones [7].

Various attempts were made to polymerize DVI using acid-catalyzed initiation, a similar procedure to that of Overberger, Montaudo, and Ishida [3]. On addition of a catalytic amount of concentrated sulfuric acid to a solution of DVI in acetone, an immediate precipitation occurred and a strong smell of acetaldehyde came from the mouth of the Pyrex tube. The precipitate had an IR spectrum different than DVI but almost identical to that of imidazolid-2-one. Controlled hydrolysis of DVI gave acetaldehyde (characterized as acetaldehyde 2, 4-dinitrophenylhydrazone) and imidazolid-2-one. From these and later results (Table 5), it would seem unlikely that DVI could be polymerized using acid-catalyzed initiation as hydrolysis to the corresponding urea and acetaldehyde would be a major competing

TABLE 1. Polymerization of 1,3-Divinylimidazolid-2-one

| Wt of monomer (g) | Solvent (% w/w) | Initiator | Mole % | Time (hr) | Temperature (°C) | Conversion[a] (%) |
|---|---|---|---|---|---|---|
| 0.5 | Toluene (5) | $BF_3$[b] | - | 5 | -80 | 31 |
| 0.5 | - | DTBP[c] | 1.41 | 3 | 130 | 90 |
| 0.5 | Toluene (10) | $BF_3 OEt_2$ | 22.6 | 5 | -50 | 62 |
| 0.5 | Benzene (20) | ABIN[d] | 2.0 | 3 | 70 | 47 |
| 0.5 | Benzene (20) | DBP[e] | 2.0 | 3 | 70 | - |

[a]Estimated gravimetrically.
[b]10 ml of $BF_3$ gas injected into sample.
[c]Ditertbutyl peroxide.
[d]Azobisisobutyronitrile.
[e]Dibenzoyl peroxide.

reaction. In view of this, it is difficult to appreciate how Overberger et al. [3] can propose that acid catalysis produces linear, soluble polymers for several N-vinylureas. Hart [8] reported that moisture in the atmosphere was sufficient to hydrolyze N-isopropenylurea to acetone and urea!

These polymerizations represent a wider variety of attempts to obtain soluble polymers and confirm the results of Crawshaw and Jones [6] indicating the failure of this monomer to cyclopolymerize.

Polymerization of 1,3-divinylhexahydropyrimid-2-one (DVHHP) was accomplished using a variety of initiators (Table 2).

As with the polymers obtained from DVI the products were insoluble in a variety of solvents, infusible up to 360° and contained residual unsaturation, evident from the infrared spectrum. Again, addition of catalytic amounts of concentrated sulphuric acid caused hydrolysis to 2-ketohexahydropyrimidine and acetaldehyde, rather than polymerization. The monomer is sufficiently sensitive to acidic conditions to be hydrolysed by N/100 hydrochloric acid.

Many attempts were made to polymerize DPDVU, but in every case no product was obtained on pouring the reaction mixture into vigorously stirred ether or light petroleum. In each attempt the monomer was recovered almost quantitatively from the reaction. The inability of DPDVU to polymerize can be explained by considering the radical formed from the monomer. Addition of an initiating radical to DPDVU produces a highly resonance-stabilized radical (III). Kharash, Kane, and Brown [9] proposed that the stability of free radicals could be equated to delocalization, i.e., resonance stability of the radicals. Such an extensive delocalizzation through the proposed conjugated system and the phenyl rings should be so stable as to prevent propagation with further molecules of DPDVU. Some evidence to support this explanation is cited later.
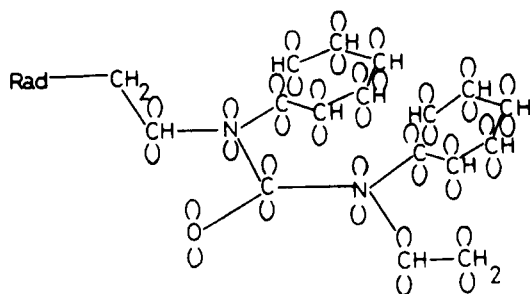
III

TABLE 2. Polymerization of 1,3-Divinylhexahydropyrimid-2-one

| Wt of monomer (g) | Solvent (% w/w) | Initiator | Mole % | Time (hr) | Temperature (°C) | Conversion[a] (%) |
|---|---|---|---|---|---|---|
| 0.5 | Toluene (5) | $BF_3$[b] | - | 5 | -80 | 26 |
| 0.5 | - | DTBP[c] | 1.54 | 3 | 130 | 72 |
| 0.5 | Toluene (10) | $BF_3 OEt_2$ | 24.6 | 5 | -50 | 53 |
| 0.5 | Benzene (20) | ABIN[d] | 2.0 | 3 | 70 | 39 |
| 0.5 | Benzene (20) | DBP[e] | 2.0 | 3 | 70 | - |

[a]Estimated gravimetrically.
[b]10 ml of $BF_3$ gas injected into sample.
[c]Ditertbutyl peroxide.
[d]Azobisisobutyronitrile.
[e]Dibenzoyl peroxide.

Many attempts to polymerize DMDVU were made without success.
In each case the monomer was recovered almost quantitatively from
the reaction.  It is difficult to explain the failure of DMDVU to polym-
erize.  Other workers have reported that certain N-vinylureas could
not be polymerized; N-vinyl-N', N'-diethylurea [3]; N-vinyl-N',N'-
methylphenylurea and N-isopropenyl-N'-phenylurea [8] failed to
give polymers with a variety of initiators.  Overberger et al. [3]
suggest that this is due to disubstitution on the nonvinylic nitrogen
atoms.  Hart [8] offers no explanation for the inability of the unsat-
urated ureas to polymerize.  Molecular models indicate that if the
nitrogen atoms are sp$^2$ hybridized (which would be necessary for the
proposed overlap) and conjugated with an sp$^2$ hybridized carbonyl
group, and the vinyl groups are also conjugated with the sp$^2$ hybrid-
ized N—CO—N system, there are two important conformations for
DMDVU (IV and V).  Conformation IV has cis arrangements of the
two methyl groups (a) and (b), and trans, trans positions of the
vinyl groups (a) and (b) with respect to the carbonyl group.  The
other conformation (V) has a trans arrangement of the methyl
groups on the nitrogen atoms with vinyl group (a) trans to the



IV



V
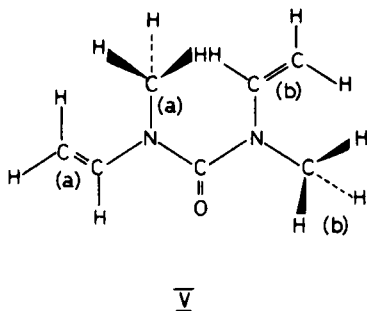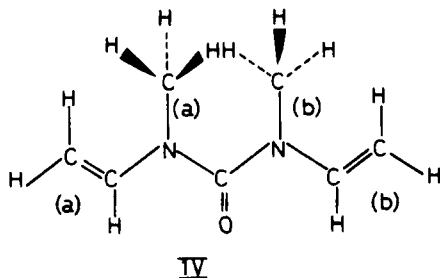
carbonyl group and vinyl group (b) cis to methyl group (b). In
IV the methyl groups (a) and (b) interact if bonds to the nitrogen
atom are in the same plane; a more stable conformation may
be found by rotation about the N—CO—N bonds to reduce this
interaction. This, of course, would reduce the degree of overlap
of the orbitals which make up the conjugated system. In V the
vinyl (b) and methyl (a) groups would similarly interact. Either
conformation would be unfavorable for intramolecular reaction
(cyclopolymerization) and it would appear that the methyl groups are
hindering the intermolecular reaction. In the cyclic ureas (DVI and
DVHHP) these groups are held back by the ring of which they are a
part, thus allowing polymerization to proceed.

The polymerization of EVI was achieved using various initiators,
the results and conditions being summarized in Table 3. The
polymers were isolated from the polymerization reaction by dropwise
addition into vigorously stirred ether or light petroleum. All the
polymers had softening points between 165 and 185°C. No acid-
catalyzed polymerizations were attempted in view of the ease of
hydrolysis of the N-vinyl group in the N, N'-divinylureas.

The IR and NMR spectra of poly(EVI) showed no residual unsatur-
ation. The polymers were soluble in a variety of solvents; benzene,
toluene, water and N, N-dimethylformamide, for example. These
facts, supported by the fusibility of the polymer, suggest a linear
structure with repeating groups as expected for a vinyl monomer (VI).

Poly(EVI) forms complexes with polybasic acids such as tannic
acid. These complexes are water insoluble, but the reaction can be
reversed by neutralizing the polyacid with base. This property of
complex formation is found for poly(N-vinylpyrrolid-2-one) which
forms complexes with iodine, polybasic acids, toxins, and drugs.
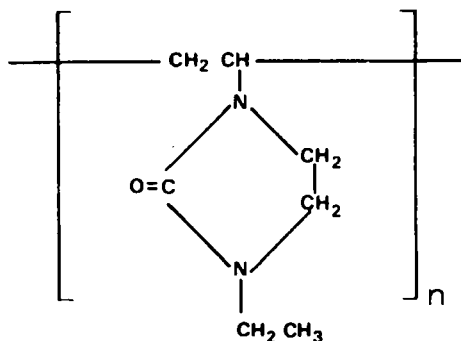


(VI)

TABLE 3. Polymerization of 1-Ethyl-3-vinylimidazolid-2-one

| Wt of monomer (g) | Solvent (% w/w) | Initiator | mole % | Time (hr) | Temperature (°C) | Conversion[a] (%) | Reduced specific viscosity,[b] $\eta_{sp}/c$ |
|---|---|---|---|---|---|---|---|
| 0.75 | - | DTBP[e] | 1.6 | 2 | 140 | 86 | - |
| 0.5 | - | ABIN[f] | 2.0 | 4 | 70 | 50 | 0.145 |
| 0.5 | Benzene (20) | ABIN | 2.0 | 4 | 70 | 38 | 0.09 |
| 0.9 | Benzene (20) | ABIN | 1.5 | 24 | 70 | 83 | 0.16 |
| 1.0 | Benzene (25) | ABIN | 1.75 | 4 | 70 | 46 | 0.19[c] |
| 2.0 | - | ABIN + $h\nu$ | 0.8 | 2 | 25 | 90 | 0.208[d] |
| 0.75 | Toluene (10) | $BF_3OEt_2$ | 10.3 | 5 | -50 | 86 | 0.114[d] |

[a]Estimated gravimetrically by precipitation in ether.
[b]For toluene solutions.
[c]Intrinsic viscosity.
[d]For aqueous solutions.
[e]Ditertbutyl peroxide.
[f]Azobisisobutyronitrile.

Poly(N-vinylpyrrolid-2-one) has been extensively studied as a plasma volume expander for use in the control of shock due to excessive blood loss, extensive burns, or dehydration [10]. Due to the similarity with poly(N-vinylpyrrolid-2-one), poly(EVI) could be a possible substitute plasma expander.

## SPECTROSCOPIC INVESTIGATION

To explain the inability of the various N,N'-disubstituted-N,N'-divinylureas to produce cyclopolymers, it has been proposed [6] that conjugation of the lone pair electrons on the nitrogen atoms with the vinyl and carbonyl double bonds produces a coplanar arrangement of these groups (II). Naturally, therefore, electronic absorption spectroscopy should make an important contribution to an investigation of the structure of these compounds. The UV absorption spectra of a number of substituted ureas have been recorded; $\lambda_{max}$ and $\epsilon_{max}$ values are given in Table 4.

All of the N,N'-divinylureas which have been studied have a strong

TABLE 4. Ultraviolet Data of Some Substituted Ureas[a]

| No. | Compound | $\lambda_{max}$ | $\epsilon_{max}$ |
|---|---|---|---|
| 1 | 1,3-Divinylimidazolid-2-one | 251 | 37600 |
| 2 | 1-Ethyl-3-vinylimidazolid-2-one | 230 | 20800 |
| 3 | 1,3-Diacetylimidazolid-2-one | 227[b] | 25500[b] |
| 4 | 1-Acetylimidazolid-2-one | 215[b] | 13000[b] |
| 5 | 1-Formylimidazolid-2-one | 214[b] | 14250[b] |
| 6 | 1,3-Diphenylimidazolid-2-one | 266 | 37000 |
| 7 | 1,3-Dibenzylimidazolid-2-one | 260 | 400 |
| 8 | 1,3-Divinylhexhydropyrimid-2-one | 248 | 40800 |
| 9 | 1,3-Dimethyl-1,3-divinylurea | 245 | 15700 |
| 10 | 1,3-Diphenyl-1,3-divinylurea | 253 | 18200 |
| 11 | 1,3-Diethyl-1,3-diphenylurea | 247[c] | 8700[c] [11] |
| 12 | 1-Phenyl-3-vinylurea | 250 | 38000 [12] |
| 13 | 1-Ethyl-3-phenylurea | 240[c] | 10900[c] [11] |
| 14 | 1,3-Diphenylurea | 256[c] | 37200[c] [11] |

[a]Recorded in methanol unless otherwise stated.
[b]Recorded in water.
[c]Recorded in ethanol.

absorption band in the UV region of the spectrum (compounds 1, 8, 9, and 10 in Table 4). The position and intensity of the bands are unlike those of isolated chromophores of the type contained in these compounds, which is good evidence that conjugation of the electron pairs on the nitrogen atoms with the $\pi$-electrons of the vinyl and carbonyl double bonds is responsible for the UV absorption of N, N'-divinylureas. Such an overlap needs some degree of coplanarity to be successful, which would explain the inability of these compounds to cyclopolymerize. The conjugation prevents the second vinyl group in an initiated molecular from adopting a conformation suitable for the intramolecular cyclization reaction.

That the vinyl groups are involved in this conjugation is shown by the fact that when a vinyl group on an imidazolid-2-one ring is replaced by an ethyl group, there is a hypsochromic shift and a hypochromic effect on the extinction coefficient (compare compounds 1 and 2, Table 4). Although the data were recorded in different solvents, a similar effect is found in the N, N'-diphenylurea system (compounds 10 and 11) and the derivatives of phenylurea (compounds 12 and 13).

Other unsaturated groups (acetyl, formyl, or phenyl) attached to the nitrogen atoms in ureas are also found to be conjugated with the carbonyl of the urea group. 1,3-Diacetylimidazolid-2-one has a strong absorption band which is modified by removal of one of the acetyl groups (compounds 3 and 4). 1-Formylimidazolid-2-one (compound 5) has a absorption spectrum similar to 1-acetylimidazolid-2-one. 1,3-Diphenylimidazolid-2-one (compound 6) has a strong absorption band which is again attributed to conjugation of the aromatic rings with the urea carbonyl group via the nitrogen atoms. In 1,3-dibenzylimidazolid-2-one (compound 7) the aromatic rings cannot be conjugated with the urea carbonyl group because of the presence of the methylene groups. Here the data are typical of two isolated aromatic rings. A comparison of compounds 13 and 14 is further evidence that a decrease in the number of unsaturated groups attached to the nitrogen atoms results in a hypsochromic effect on the extinction coefficient.

If the hydrogen atoms attached to the nitrogens of 1,3-diphenylurea (compound 14) are replaced by ethyl groups (compound 11), there is a considerable change in the spectrum which indicates that there is a diminished interaction between the $\pi$-orbitals of the aromatic rings and the urea group. This seems to be a steric effect due to the presence of the relatively bulky ethyl groups. The aromatic rings are unable to take up a planar conformation because of overcrowding in the molecule. Presumably the steric strain is relieved by twisting the essentially single bond between the aromatic ring and the nitrogen atoms and/or the essentially single bond in the urea group.

Since there is a considerable hypsochromic shift and a large decrease
in absorption intensity, the departure from coplanarity must be sig-
nificant. The crystal structure of 1,3-diethyl-1,3-diphenylurea has
been studied by x-ray diffraction [13]. Both phenyl groups are trans
with respect to the oxygen atom, and nonbonded interactions between
the phenyl groups are relaxed both through a rotation of the phenyl
rings around the bonds joining them to the nitrogen atoms and through
a displacement of these bonds out of the plane of the urea group in
opposite directions. The hybridization of the nitrogen atom is inter-
mediate between trigonal and tetrahedral. This result is in agreement
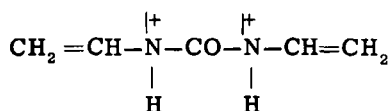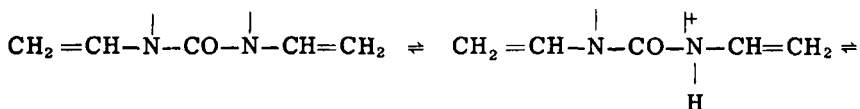with the picture presented by our UV data.

In DPDVU (compound 10) the introduction of vinyl groups to replace
ethyl groups produces, as expected, a bathochromic shift and has a
hyperchromic effect on the extinction coefficient. There is certainly
an increase in conjugation in the system. However, the position and
intensity of the absorption band indicates the overlap of orbitals is not
as successful as in 1,3-diphenylurea (compound 14). The spectrum
of DPDVU (compound 10) suggests that the molecule does not adopt a
conformation with either the two phenyl groups or the two vinyl groups,
or one phenyl and one vinyl group coplanar with the urea group
(carbonyl). The intensity of the absorption band is far less than those
of compounds 14, 6, 1, 8, or 12. However, it does show that there is
considerable conjugation in this molecule which would support the
proposal that a resonance stabilized radical is responsible for its in-
ability to polymerize (III).

1,3-Diphenylimidazolid-2-one (compound 15) has a similar ab-
sorption spectrum to 1,3-diphenylurea (compound 14), which suggests
that the phenyl groups can assume a conformation coplanar with the
cyclic urea group. Thus the steric effect of substituents on the nitrogen
atoms is removed if they are part of a five-membered ring system.
Since compounds 1 and 8 have similar absorption bands, the same
effect is found if the substituents are part of a six-membered ring.

In DMDVU (compound 9), the absorption spectrum indicates that
there is a conjugated system but that it is unable to take up a com-
pletely planar conformation because of overcrowding of the groups at-
tached to the nitrogen atoms. This departure from coplanarity effects
the position and intensity of the absorption band of the conjugated
system compared to DVI and DVHHP. Two possible conformations for
DMDVU molecules have been proposed. In either conformation, steric
interactions involving the methyl groups would explain the lack of
coplanarity in the conjugated system.

The absorption spectra of DVI and DVHHP were recorded in
solutions of varying pH values. The spectra were found to be pH
dependent; lowering the pH caused the absorption bands to diminish

and finally disappear. This was considered to reflect the equilibrium between the free N, N'-divinylurea and the nitrogen-protonated species:

$$CH_2 =CH-\overset{|}{N}-CO-\overset{|}{N}-CH=CH_2 \rightleftharpoons CH_2 =CH-\overset{|}{N}-CO-\overset{|+}{\underset{|}{N}}-CH=CH_2 \rightleftharpoons$$
$$H$$

$$CH_2 =CH-\overset{|+}{\underset{|}{N}}-CO-\overset{|+}{\underset{|}{N}}-CH=CH_2$$
$$H \quad\quad H$$

However, it was soon apparent that the spectra were also time dependent. The absorption bands diminished and disappeared on leaving acidic solutions of the ureas standing. The rate of disappearance of the band was dependent upon the pH of the solution; in solutions of low pH the peak diminished at a greater rate than in solutions of higher pH. After standing for several days, even aqueous (neutral) solutions of these N, N'-divinylureas were found to have no UV absorption band at the position where they previously had an intense absorption. This led to the suggestion that hydrolysis of the N-vinyl group was occurring:

$$CH_2 =CH-\overset{|}{N}-CO-\overset{|}{N}-CH=CH_2 + 2H_2 O \longrightarrow 2CH_3 CHO + H\overset{|}{N}-CO-\overset{|}{N}H$$
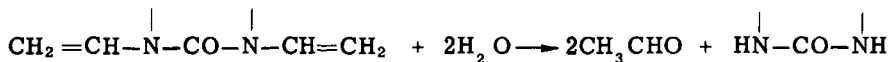
Controlled hydrolysis of these ureas did yield acetaldehyde and the corresponding urea. The UV absorption maxima of acidic solutions of both DMDVU and EVI were also found to decrease with time due to hydrolysis of the N-vinyl groups.

A dilute acid solution (pH 3.5), which caused rapid hydrolysis of the other N-vinylureas, had no immediate effect on the absorption spectrum of DPDVU. However, increasing the strength of the acid solution to 2 $\underline{M}$ caused the absorption at 253 nm to increase. The equilibrium absorbance value corresponded to a molar extinction coefficient, $\epsilon$ = 28,000, based on DPDVU. The increase in absorbance is consistent with the proposal that hydrolysis would produce 1, 3-diphenylurea, which has an $\epsilon$-value of 37,000 compared with 18,200 for DPDVU (Table 4). The value $\epsilon$ = 28,000 is based on DPDVU; if

this value is modified by using the molecular weight for 1, 3-diphenylurea in the calculation, then the $\epsilon$-value becomes 35,000, which compares very well with the value 37,000 for 1, 3-diphenylurea in ethanol [11]. Apart from steric effects, the difference is reactivity between DPDVU and the other N-vinylureas may be interpreted in terms of resonance stabilization by the phenyl groups on the N-vinyl-urea structure, thus lowering the nucleophilic reactivity of the $\beta$-carbon atoms and the basicity of the nitrogen atoms.

As both DVI and DVHHP have intense UV absorption bands, the rate of disappearance of the absorption band can be used as a measure of the rate of hydrolysis. Hydrolysis data exhibited first-order kin-etics. Since the change in the buffer concentration is negligible compared with the change in urea concentration, the reaction order is termed pseudo-first-order. Table 5 gives the pseudo-first-order rate constants for the hydrolysis of DVI and DVHHP. The data in Table 5 shows that the N, N'-divinylureas are rapidly hydrolyzed by dilute acidic solutions. At pH 4.10, DVI has a half-life of approximately 320 sec, which means that 50% of the urea will be hydrolyzed in about 5 min. This is much faster than the rate of hydrolysis of N-vinyl-pyrrolid-2-one; 1% hydrolysis over 6 hr at pH 5. These results indicate that it is not practicable to polymerize the N, N'-divinylureas studied in aqueous solutions because of the rate at which hydrolysis takes place.

The rates of hydrolysis of DVI and DVHHP were measured at two temperatures in solutions with a constant pH value (Table 6). Table 7 shows the entropies and enthalpies of activation, calculated from the data. The data show that the $\Delta S^{\oplus \ddagger}$ value is important in the hydrolysis of these N, N'-divinylureas. Although the activation energy for the hydrolysis of the five-membered ring urea is higher than that for the

TABLE 5. Pseudo-First-Order Rate Constants in Constant Ionic Strength Buffers of 1, 3-Divinylimidazolid-2-one and 1, 3-Divinylhex-ahydropyrimid-2-one at 25 ± 0.1°

| pH | Rate constants of 1, 3-divinylimidazolid-2-one (DVI), $(k \times 10^3)/sec^{-1}$ | Rate constants of 1, 3-divinylhexahydropyrimid-2-one (DVHHP), $(k \times 10^3)/sec^{-1}$ | $\dfrac{DVI}{DVHHP}$ |
|---|---|---|---|
| 4.10 | 1.07 | 0.70 | 1.53 |
| 3.80 | 2.06 | 1.24 | 1.66 |
| 3.40 | 4.36 | 2.60 | 1.67 |

TABLE 6. Pseudo-First-Order Rate Constants in Constant Ionic Strength Buffers of 1,3-Divinylimidazolid-2-one and 1,3-Divinyl-hexahydropyrimid-2-one at Various Temperatures

| Temperature (°C) | pH | Rate constants of 1,3-divinylimida-zolid-2-one (DVI) $(k \times 10^3)/\text{sec}^{-1}$ | Rate constants of 1,3-divinylhexahy-dropyrimid-2-one (DVHHP) $(k \times 10^3)/\text{sec}^{-1}$ | $\dfrac{\text{DVI}}{\text{DVHHP}}$ |
|---|---|---|---|---|
| 40 | 4.80 | 0.80 | - | |
| 41 | 4.80 | - | 0.73 | |
| 50 | 4.80 | 1.59 | 1.13 | 1.41 |

TABLE 7. Entropies and Enthalpies of Activation for the Hydrolysis of 1,3-Divinylimidazolid-2-one and 1,3-Divinylhexahydropyrimid-2-one

| | $\Delta H^{\ominus\ddagger}$ (kJ/mole) | $\Delta S^{\ominus\ddagger}$ [J/(mole)(deg)] |
|---|---|---|
| 1,3-Divinylimidazolid-2-one | 57.3 | 83 |
| 1,3-Divinylhexahydropyrimid-2-one | 40.6 | 142 |

six-membered ring urea, DVI hydrolyses approximately one and a half times faster than DVHHP.

Stamhuis [14] found that the rates of hydrolysis of pyrrolidino enamines were much greater than the corresponding piperidino compounds, despite the fact that the basicities were very similar. Stamhuis suggests that the five-membered ring enamine forms an exocyclic double bond more easily than the corresponding six-membered ring enamine. This is found in other reactions of these enamines with electrophilic reagents [15, 16]. Similarly, these results show that DVI, a five-membered ring N,N'-divinylurea, is more reactive in hydrolysis reactions than DVHHP, a six-membered ring N,N'-divinylurea.

Nuclear magnetic resonance spectroscopic data has been used to indicate the degree of overlap between the electron pair on the nitrogen

atom and the vinylic double bond in certain enamines. It is suggested that the higher the field at which the vinylic proton absorbs [17, 18] the greater is the degree of p-$\pi$ overlap. A similar effect is observed for the chemical shift values of the N$-$C$\underline{H}$=CH$_2$ protons in N-vinylureas, which are given in Table 8, together with their UV absorption intensity. These results also seem to indicate that the greater the p-$\pi$ overlap, the lower the chemical shift for the N$-$C$\underline{H}$=CH$_2$ protons. On the basis of their UV absorption spectra, compounds 1, 2, and 3 exhibit a greater degree of p-$\pi$ overlap than compounds 4 and 5.

The high intensity of the C=C stretching vibration in the IR spectra of enamines has been attributed to the overlap of electrons on the nitrogen atom and the $\pi$-electrons of the double bond. The IR absorption band attributed to the ring carbonyl and the UV absorption intensity for some N,N'-disubstituted imidazolid-2-ones are given in Table 9. The data in Table 9 indicate that the carbonyl absorption frequency of imidazolid-2-one is shifted to a higher frequency on substitution with a group which can be conjugated with the carbonyl group via the nitrogen atom. Compare $\nu_{C=C}$ for compound 1 with compounds 7 and 8 and compare compound 2 with compound 5. The effect also appears to be additive; two substituents causing a greater frequency shift than does one substituent. Compare compounds 1, 8, and 9 and compounds 2, 5, and 6. This effect correlated with the extinction coefficients of the UV absorption bands (and hence degree of conjugation).

For 1, 3-diethylimidazolid-2-one (compound 2), EVI (compound 5), and DVI (compound 6), the increase in conjugation is in the order, 2 < 5 < 6. This increase in conjugation reduces the availability of

TABLE 8. Chemical Shift Values of the N$-$C$\underline{H}$=CH$_2$ Protons in some N-Vinylureas    .

| No. | Compound | Chemical shift of C$\underline{H}$=CH$_2$ protons, $\tau$ | Ultraviolet[a] absorption, $\epsilon_{max}$ |
|-----|----------|------|------|
| 1 | 1, 3-Divinylhexahydropyrimid-2-one | 2.3-2.7 | 40, 800 |
| 2 | 1, 3-Divinylimidazolid-2-one | 2.8-3.3 | 37, 600 |
| 3 | 1-Ethyl-3-vinylimidazolid-2-one | 2.8-3.3 | 20, 800 |
| 4 | 1, 3-Diphenyl-1, 3-divinylurea | 3.3-3.5 | 18, 200 |
| 5 | 1, 3-Dimethyl-1, 3-divinylurea | 3.2-3.7 | 15, 700 |

[a]Values taken from Table 4.

TABLE 9. Carbonyl Infrared Absorption Frequencies and Ultraviolet Extinction Coefficients of Some Substituted Imidazolid-2-ones

| No. | Compound | $\epsilon_{max}$[a] | $\nu_{C=O}$[b] (cm$^{-1}$) | $\nu_{C=O}$' literature values (cm$^{-1}$) |
|---|---|---|---|---|
| 1 | Imidazolid-2-one | - | 1660 | 1661 [20]; 1660 [21] |
| 2 | 1,3-Diethylimidazolid-2-one | - | 1685[c] | - |
| 3 | 1,3-Dibenzylimidazolid-2-one | 400 | 1685 | - |
| 4 | 1,3-Diphenylimidazolid-2-one | 37,000 | 1690 | 1690 [7] |
| 5 | 1-Ethyl-3-vinyl-imidazolid-2-one | 20,800 | 1705[c] | - |
| 6 | 1,3-Divinyl-imidazolid-2-one | 37,600 | 1725 | 1715-1725 [6] |
| 7 | 1-Formylimidazolid-2-one | 14,250 | 1725 | - |
| 8 | 1-Acetylimidazolid-2-one | 13,000 | 1750 | 1750 [20]; 1740 [19]; 1749 [22] |
| 9 | 1,3-Diacetylimidazolid-2-one | 25,500 | 1755 | 1750; 1760 [20]; 1759 [19] |

[a]Taken from Table 4.
[b]Potassium bromide disk unless otherwise stated.
[c]Liquid film.

electrons at the nitrogen atoms, and hence the ring carbonyl frequencies increase with increasing conjugation. Similar effects have been observed for other N,N'-divinylureas, and the results are shown in Table 10 along with the data for some analogous saturated ureas. Again a system with conjugation shows an increase in carbonyl absorption frequency over a nonconjugated system. The changes in

TABLE 10. Carbonyl Infrared Absorption Frequencies of Some Substituted Ureas

| Compound | $\nu_{C=O}{}^{a}$ (cm$^{-1}$) |
|---|---|
| 1,3-Dimethyl-1,3-divinylurea | 1665[b] |
| 1,1,3,3-Tetramethylurea | 1640[b] |
| 1,3-Diphenyl-1,3-divinylurea | 1675 |
| 1,3-Diphenylurea | 1660 |
| 1,3-Dimethyl-1,3-diphenylurea | 1635 [23] |
| 1,3-Divinylhexahydropyrimid-2-one | 1665 |
| 1,3-Diethylhexahydropyrimid-2-one | 1645[b] |
| 1,3-Divinylurea | 1660 [7] |
| 1,3-Dimethylurea | 1640 |

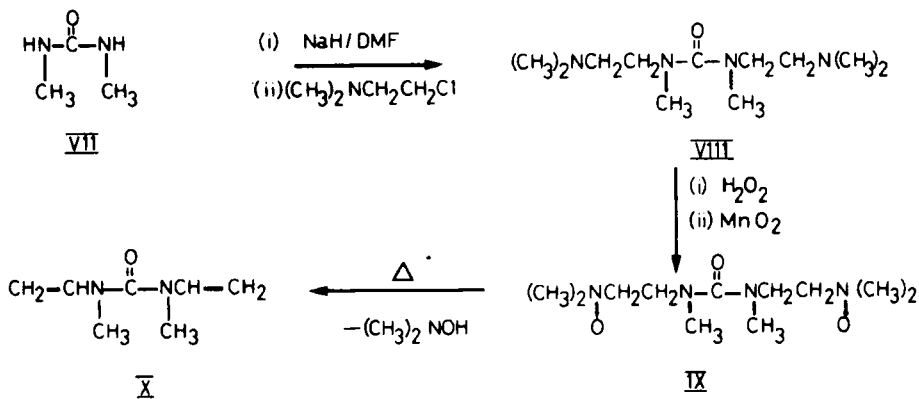[a]Potassium bromide disk unless otherwise stated.
[b]Liquid film.

carbonyl frequencies are less marked in these examples than in the five-membered ring imidazolid-2-one series (Table 9).

## EXPERIMENTAL

1,3-Divinylimidazolid-2-one, 1,3-divinylhexahydropyrimid-2-one, and 1,3-diphenyl-1,3-divinylurea were prepared by the methods of Crawshaw and Jones [6]. 1,3-Dimethyl-1,3-divinylurea was prepared from 1,3-dimethylurea via a Cope elimination (VII-X). 1-Ethyl-3-vinylimidazolid-2-one was prepared from 1-ethylimidazolid-2-one [24-28] via a Hofmann degradation reaction (XI-XV).

## 1,3-Bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (VIII)

Dry 1,3-dimethylurea (15.0 g, 0.17 mole) was dissolved with stirring in anhydrous N,N-dimethylformamide (200 ml) in a flask equipped with an efficient reflux condenser topped with a solid carbon dioxide/acetone cold finger. Sodium hydride (60% dispersion in oil, 20.0 g) was added with stirring, followed by dropwise addition of N,N-dimethyl-2-chloroethylamine (39.6 g, 0.37 mole). The mixture was heated to 60°C

HN–C–NH with CH₃ CH₃ — VII

(i) NaH/DMF
(ii) (CH₃)₂NCH₂CH₂Cl

(CH₃)₂NCH₂CH₂N–C–NCH₂CH₂N(CH₃)₂ with CH₃ CH₃ — VIII

(i) H₂O₂
(ii) MnO₂

(CH₃)₂NCH₂CH₂N–C–NCH₂CH₂N(CH₃)₂ — IX

Δ
–(CH₃)₂NOH

CH₂=CHN–C–NCH=CH₂ with CH₃ CH₃ — X

(XI) HN–NCH₂CH₃ (i) NaH/DMF (ii)(CH₃)₂NCH₂CH₂Cl → (CH₃)₂NCH₂CH₂N ... NCH₂CH₃ — XII

CH₃I

(XIII) (CH₃)₂⁺NCH₂CH₂N ... NCH₂CH₃ I⁻

Ag₂O

(XIV) (CH₃)₃⁺NCH₂CH₂N ... NCH₂CH₃ OH⁻

Δ –H₂O –(CH₃)₃N

(XV) CH₂=CHN ... NCH₂CH₃

on a water bath when a vigorous exothermic reaction commenced. After the initial reaction had subsided, the solution was maintained at 90 to 95°C for a further 20 hr. The solution was cooled, poured into dilute hydrochloric acid (1200 ml), and extracted with chloroform to remove the oil introduced with the sodium hydride. The aqueous layer was made alkaline with aqueous sodium hydroxide (30% w/v), extracted

with chloroform, and the extract dried over anhydrous calcium chloride. Chloroform was removed under reduced pressure to give 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (28.1 g, 72%) as a deep red liquid; $\nu_{max}$ 2950(C—H), 1680(C=O), 1262 cm$^{-1}$(amide III), characterized as dimethiodide since distillation caused decomposition.

## Dimethiodide of 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea

Methyl iodide (8.5 g, 0.06 mole) in anhydrous ether (50 ml) was added dropwise over 1 hr to a solution of 1,3-bis(N,N-dimethylamino-ethyl)-1,3-dimethylurea (6.9 g, 0.03 mole) in anhydrous ether (75 ml). The precipitated solid was crystallized giving the dimethiodide of 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (12.3 g, 80%) mp 224 to 225°C (white needles from methanol).

Analysis. Found: C, 30.2; H, 6.3; N, 10.8%. $C_{13}H_{32}N_4OI_2$ requires:    C, 30.35; H, 6.25; N, 10.9%; $\nu_{max}$ 2900(C—H), 1620(C=O), 1315 cm$^{-1}$(amide III); $\tau$(D$_2$O), 6.4(8H, s, CO—N—CH$_2$—CH$_2$—$\overset{+}{N}$), 6.8(18H, s, $\overset{+}{N}$(CH$_3$)$_3$), 7.0(6H, s, CH$_3$—N—CO—N—CH$_3$).

## 1,3-Dimethyl-1,3-divinylurea (X)

1,3-Bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (23.0 g, 0.1 mole) was dissolved in methanol (150 ml), cooled to 5°C, and hydrogen peroxide (100 vol, 60 g) was added dropwise with stirring over 1 hr. The solution was allowed to warm to room temperature and stirring maintained for 15 hr, after which time the solution no longer turned phenolphthalein paper red. Manganese dioxide (1.0 g) was added and the solution stirred until the supernatant liquid did not color starch iodide paper. The solution was filtered and water and methanol removed under reduced pressure. The syrupy product was distilled and the fraction bp 80 to 100°C at 5.0 Torr collected. Distillation was stopped immediately since further heating invariably caused the residue to explode ! Redistillation from solid sodium hydroxide yielded 1,3-dimethyl-1,3-divinylurea (4.1 g, 29%), bp 52 to 54°C at 1.0 Torr as a colorless liquid, $n_D^{25}$ 1.5067.

Analysis. Found: C, 60.25; H, 8.75; N, 20.1%; M$^+$, 140. $C_7H_{12}N_2O$ requires: C, 60.05; H, 8.7; N, 20.05%; M, 140; $\nu_{max}$ 3100(C—H), 2910(C—H), 1675(C=O), 1270(amide III), 1320, 978, 845 cm$^{-1}$ (N—CH=CH$_2$); $\tau$(CCl$_4$), 3.2-3.7(2H, q, N—CH=CH$_2$), 5.7-6.1 (4H, t, N—CH=CH$_2$), 7.1(6H, s, N—CH$_3$); $\lambda_{max}$ 245 nm($\epsilon$ 15,700).

## 1-Ethyl-3-(N,N-dimethylaminoethyl)imidazolid-2-one (XII)

1-Ethylimidazolid-2-one (19.4 g, 0.17 mole) was dissolved with stirring in anhydrous N,N-dimethylformamide (200 ml) in a flask equipped with an efficient reflux condenser topped with a solid carbon dioxide/acetone cold finger. Sodium hydride (60% dispersion in oil, 10.0 g) was added with stirring followed by dropwise addition of N,N-dimethyl-2-chloroethylamine (19.8 g, 0.185 mole). The mixture was heated to 60°C when a vigorous exothermic reaction commenced. After the initial reaction had subsided the solution was maintained at 90 to 95°C for a further 8 hr. The mixture was cooled, poured into water (1000 ml), and extracted with chloroform. The extract was dried over anhydrous calcium chloride and the chloroform was removed under reduced pressure yielding 1-ethyl-3-(N,N-dimethyl-aminoethyl)imidazolid-2-one (26.4 g, 81%) as a deep red liquid; $\nu_{max}$ 2800(N—(CH$_3$)$_2$), 1690(C=O), 1270 cm$^{-1}$(amide III).

## Methiodide of 1-Ethyl-3-(N,N-dimethylaminoethyl) imidazolid-2-one (XIII)

Methyl iodide (17.0 g, 0.12 mole) in anhydrous ether (50 ml) was added dropwise over 1 hr to a solution of 1-ethyl-3-(N,N-dimethyl-aminoethyl)imidazolid-2-one (19.8 g, 0.12 mole) in anhydrous ether (200 ml). The precipitate was crystallized giving the methiodide of 1-ethyl-3-(N,N-dimethylaminoethyl)imidazolid-2-one (34.0 g, 86%) mp 200 to 201°C (white needles from methanol).

Analysis. Found: C, 36.4; H, 7.0; N, 12.4%. C$_{10}$H$_{22}$H$_3$OI requires: C, 36.7; H, 6.8; N, 12.85%; $\nu_{max}$ 1700(C=O), 1270 cm$^{-1}$ (amide III); $\tau$(D$_2$O), 6.2-7.0(19H, m, all CH$_2$ and $\overset{+}{N}$(CH$_3$)$_3$), 8.8-9.1(3H, t, N—CH$_2$—CH$_3$).

## 1-Ethyl-3-vinylimidazolid-2-one (XV)

The methiodide of 1-ethyl-3(N,N-dimethylaminoethyl)imidazolid-2-one (32.7 g, 0.1 mole) was dissolved in a mixture of ethanol (200 ml) and water (60 ml). Silver oxide (23.2 g, 0.1 mole) was added and the mixture stirred at 40°C until the supernatant liquid was free from iodide ions. The solution was filtered and water and ethanol were re-moved under reduced pressure to give the quaternary ammonium hydroxide as a pale yellow syrup. The syrup was decomposed at 120

to 130°C at 1.5 Torr yielding 1-ethyl-3-vinyl-imidazolid-2-one (9.0 g, 64%), bp 116 to 118°C at 1.5 Torr as a colorless liquid $n_D^{25}$ 1.4991.

Analysis. Found: C, 60.1; H, 8.9; N, 20.2%; $M^+$, 140. $C_7H_{12}N_2O$ requires: C, 60.05; H, 8.7; N, 20.05%; M, 140; $\nu_{max}$ 3120(C—H vinyl), 2990-2900(C—H), 1705(C=O), 1635(C=C), 1503(amide II), 1278(amide III), 990, 838 cm$^{-1}$ (N—CH=CH$_2$); $\tau$(CDCl$_3$), 2.8-3.3(1H, q, N—C$\underline{H}$=CH$_2$), 5.8-6.2(2H, m, N—CH=C$\underline{H}_2$), 6.6(4H, s, CH$_2$ ring), 6.6-6.9(2H, q, N—C$\underline{H}_2$—CH$_3$), 8.7-9.0(3H, t, N—CH$_2$—C$\underline{H}_3$); $\lambda_{max}$ 230 nm($\epsilon$20,000).

## Poly(1-ethyl-3-vinylimidazolid-2-one

Table 3 shows representative polymerization conditions and results. The following is a typical procedure for a free radical initiated polymerization. 1-Ethyl-3-vinylimidazolid-2-one (1.00 g, $7.14 \times 10^{-3}$ mole) was dissolved in anhydrous benzene (4.0 g) in a Pyrex tube. Azobisisobutyronitrile (20 mg, $1.22 \times 10^{-4}$ mole, 1.75 mole %) was added and the tube purged with dry nitrogen, sealed with a rubber serum cap, vigorously agitated, and placed in a thermostat bath at 70 ± 0.1°C for 4 hr. The contents of the tube were slowly added to vigorously stirred diethyl ether (200 ml). The precipitated polymer was collected by filtration, washed repeatedly with diethyl ether, and dried at 55°/0.1 Torr for 8 hr to give poly(1-ethyl-3-vinylimidazolid-2-one (0.46 g, 46%), softening point 165°C (white amorphous solid).

Analysis. Found: C, 58.9; H, 8.8; N, 18.95%. $(C_7H_{12}N_2O)_n$ requires: C, 60.05; H, 8.65; N, 20.05%; $\nu_{max}$ 2970-2900(C—H), 1690(C=O), 1503(amide II), 1270 cm$^{-1}$(amide III); $\tau$(C$_6$D$_6$), 6.3-7.2(br), 8.6-9.3(br).

## Hydrolysis of 1,3-Divinylimidazolid-2-one or 1,3-Divinylhexahydropyrimid-2-one

Hydrochloric acid (30 ml, N/100) was added to 0.20 g of 1,3-divinyl-imidazolid-2-one or 1,3-divinylhexahydropyrimid-2-one under a slow stream of dry nitrogen. The exit tube from the flask was immersed in a solution of 2,4-dinitrophenylhydrazine (alcohol/sulfuric acid). After passing nitrogen for 1 hr the precipitated 2,4-dinitrophenylhydrazone (0.35 g) was collected and crystallized to give acetaldehyde 2,4-dinitrophenylhydrazone, mp and mixed mp 166°C (orange needles from ethanol) with an identical IR spectrum to an authentic sample. Water

was removed under reduced pressure from the residual hydrolysis
mixture leaving a crystalline solid of imidazolid-2-one, mp 130 to
131°C (white needles from ethanol) having an identical IR spectrum
to an authentic sample. Similarly, 2-ketohexahydropyrimidine mp
274 to 276°C (white needles from water) having an identical IR
spectrum to an authentic sample was the residue from the hydrolysis
of 1, 3-divinylhexahydropyrimid-2-one.

## Hydrolysis of 1, 3-Diphenyl-1, 3-divinylurea

Hydrochloric acid (20 ml, 6 N) was added to 0.15 g of 1,3-
diphenyl-1,3-divinylurea under a slow stream of dry nitrogen. The
exit tube from the flask was immersed in a solution of 2, 4-dinitro-
phenylhydrazine (alcohol/sulfuric acid). After passing nitrogen for
4 hr the precipitated 2, 4-dinitrophenylhydrazone was collected and
crystallized to give acetaldehyde 2, 4-dinitrophenylhydrazone, mp
and mixed mp 166°C (orange needles from ethanol) with an identical
IR spectrum to an authentic sample. Water was removed under
pressure from the residual hydrolysis mixture leaving a white solid
of 1, 3-diphenylurea, mp and mixed mp 239 to 240°C (long white
needles from methanol) having an identical IR spectrum to an
authentic sample.

## 1-Acetylimidazolid-2-one

Imidazolid-2-one (17.4 g, 0.2 mole) was dissolved with stirring in
a mixture of acetic anhydride (21.0 g, 0.2 mole) and glacial acetic
acid (80 ml). The solution was refluxed for 4 hr, cooled, and poured
into diethyl ether (200 ml). The precipitate was crystallized giving
1-acetylimidazolid-2-one (14.6 g, 57%), mp 177 to 178°C (white
prisms from ethanol).

Analysis. Found: C, 46.6; H, 6.15; N, 21.9%; M$^+$, 128. Calculated
for $C_5H_8N_2O_2$: C, 46.9; H, 6.3; N, 21.85%; M, 128; $\nu_{max}$ 3300(N—H),
3000, 2930(C—H), 1750(C=O), 1655(C=O), 1265 cm$^{-1}$ (amide III);
$\tau$ ($D_2O$), 6.0-6.7(4H, m, ring protons), 7.7(3H, s, N—CO—CH$_3$); $\lambda_{max}$
($H_2O$), 215 nm($\epsilon$ 13,000).

## 1, 3-Diacetylimidazolid-2-one

Imidazolid-2-one (10.0 g, 0.116 mole) was dissolved with stirring
in a mixture of acetyl chloride (45.0 g, 0.574 mole) and glacial acetic

acid (50 ml). The solution was refluxed for 4 hr, cooled, and poured into diethyl ether (200 ml). The precipitate was crystallized giving 1,3-diacetylimidazolid-2-one (15.1 g, 77%), mp 126 to 127 °C (white prisms from acetone),

Analysis. Found: C, 49.6, H, 6.0; N, 16.65%; $M^+$, 170. Calculated for $C_7H_{10}N_2O_3$: C, 49.4; H, 5.9; N, 16.45%; M, 170; $\nu_{max}$ 3000-2930(C—H), 1755(C=O), 1695(C=O) 1260 cm$^{-1}$ (amide III); $\tau$(D$_2$O), 6.2(4H, s, ring protons), 7.5(6H, s, N—CO— CH$_3$); $\lambda_{max}$ (H$_2$O), 227 nm($\epsilon$ 25, 500).

## 1 - Formylimidazolid-2-one

Imidazolid-2-one (15.0 g, 0.17 mole) was dissolved with stirring in a mixture of formic acid (8.0 g, 0.17 mole) and acetic anhydride (17.0 g, 0.17 mole), refluxed for 3 hr, cooled, and poured into diethyl ether (200 ml). The precipitate was crystallized giving 1-formylimidazolid-2-one (13.2 g, 68%) mp 151 to 152°C (white prisms from acetone).

Analysis. Found: C, 42.05; H, 5.25; N, 24.75%. $C_4H_6N_2O_2$ requires: C, 42.1; H, 5.3; N, 24.55%; $\nu_{max}$ 3300(N—H), 1725(C=O), 1680(C=O), 1268 cm$^{-1}$(amide III); $\tau$(D$_2$O), 1.4(1H, s, H—C=O), 6.1-6.7(4H, m, ring protons); $\lambda_{max}$(H$_2$O), 214 nm($\epsilon$ 14, 250).

## 1, 3 - Diethylimidazolid-2-one

Imidazolid-2-one (7.5 g, 0.085 mole) was dissolved with stirring in anhydrous N,N-dimethylformamide (100 ml) in a flask equipped with an efficient reflux condenser topped with a solid carbon dioxide/acetone cold finger. Sodium hydride (60% dispersion in oil, 10.0 g) was added with stirring followed by dropwise addition of ethyl iodide (28.0 g, 0.17 mole). A vigorous exothermic reaction occurred with evolution of hydrogen. After the reaction subsided the solution was maintained at 90 °C for a further 18 hr. The solution was cooled, poured into water (600 ml), extracted with chloroform, and the extract dried over anhydrous calcium chloride. Chloroform was removed under reduced pressure and the residue distilled yielding 1,3-diethylimidazolid-2-one (8.2 g, 68%), bp 83 to 84°C at 0.5 Torr as a colorless liquid $n_D^{25}$ 1.4678.

Analysis. Found: C, 58.85; H, 10.0; N, 19.6%; $M^+$, 142. Calculated for $C_7H_{14}N_2O$: C, 59.15; H, 9.9; N, 19.7%; M, 142; $\nu_{max}$ 2970,

2870(C—H), 1685(C=O), 1263 cm$^{-1}$ (amide III); $\tau$(CCl$_4$), 6.8(4H, s, ring protons), 6.8-7.3(4H, q, N—CH$_2$—CH$_3$), 8.8-9.1 (6H, t, N--CH$_2$CH$_3$).

## 1,3-Dibenzylimidazolid-2-one

Imidazolid-2-one (7.5 g, 0.085 mole) was dissolved with stirring in anhydrous N,N-dimethylformamide (100 ml) in a flask equipped with an efficient reflux condenser topped with a solid carbon dioxide/ acetone cold finger. Sodium hydride (60% dispersion in oil, 10.0 g) was added with stirring followed by dropwise addition of benzyl chloride (22.0 g, 0.17 mole). A vigorous exothermic reaction occurred with evolution of hydrogen. After the reaction had subsided the solution was maintained at 90°C for a further 14 hr. The solution was cooled, poured into water (600 ml), and the solid which separated collected by filtration. Crystallization of the solid gave 1,3-dibenzylimidazolid-2-one (18.5 g, 82%), mp 92 to 93°C (white flakes from light petroleum, bp 60 to 80°C).

Analysis. Found: C, 76.5; H, 6.85; N, 10.5%; M$^+$, 266. Calculated for C$_{17}$H$_{18}$N$_2$O: C, 76.65; H, 6.8; N, 10.5%; M, 266; $\nu_{max}$ 3020(C—H aromatic), 2920-2860(C—H aliphatic), 1690(C=O), 1493, 1450(C=C), 1255 cm$^{-1}$(amide III); $\tau$(CS$_2$), 3.1(10H, s, phenyl protons), 5.9(4H, s, N—CH$_2$—C$_6$H$_5$), 7.1(4H, s, ring protons); $\lambda_{max}$ 260 nm ($\epsilon$ 400).

## 1,3-Diphenylimidazolid-2-one

During the synthesis of 1,3-diphenyl-1,3-divinylurea, 1,3-diphenyl-imidazolid-2-one was isolated from the reaction of N,N-dimethyl-2-chloroethylamine with the disodium salt of 1,3-diphenylurea; the major product of the reaction being 1,3-bis(N,N-dimethylaminoethyl)-1,3-diphenylurea. Crystallization gave 1,3-diphenylimidazolid-2-one (5.1 g, 12% based on diphenylurea), mp 215 to 216°C (silvery-white flakes from ethanol); $\nu_{max}$ 1680(C=O), 1300(amide III), 1598, 1498, 754, 694 cm$^{-1}$ (monosubstituted benzene); $\tau$((CD$_3$)$_2$CO), 2.1-3.0 (10H, m, phenyl protons), 6.0(4H, s, ring protons); $\lambda_{max}$, 266 nm ($\epsilon$37, 000).

## 1,3-Diethylhexahydropyrimid-2-one

2-Ketohexahydropyrimidine (8.7 g, 0.085 mole) was dissolved with stirring in anhydrous N,N-dimethylformamide (100 ml) in a flask

equipped with an efficient reflux condenser topped with a solid carbon dioxide/acetone cold finger. Sodium hydride (60% dispersion in oil, 10.0 g) was added with stirring, followed by dropwise addition of ethyl iodide (28.0 g, 0.17 mole). A vigorous exothermic reaction occurred with evolution of hydrogen. After the reaction had subsided the solution was maintained at 90°C for a further 6 hr. The solution was cooled, poured into water (600 ml), extracted with chloroform, and the extract dried over anhydrous calcium chloride. Removal of chloroform under reduced pressure followed by distillation gave 1,3-diethylhexahydropyrimid-2-one (10.1 g, 77%), bp 95 to 96°C at 0.5 Torr as a colorless liquid $n_D^{25}$ 1.4774.

Analysis. Found: C, 61.2; H, 10.15; N, 17.6%; $M^+$, 156. Calculated for $C_8H_{16}N_2O$: C, 61.5; H, 10.3; N, 17.9%; M, 156; $\nu_{max}$ 2960, 2890(C—H), 1645(C=O), 1296 cm$^{-1}$(amide III); $\tau$(CCl$_4$), 6.6-7.0 (8H, m, CH$_2$ protons adjacent nitrogen), 8.0-8.4(2H, m, N—CH$_2$—CH$_2$—C$\underline{H}_2$—N), 9.0-9.2(6H, t, N—CH$_2$—C$\underline{H}_3$).

## ACKNOWLEDGMENTS

## REFERENCES

[1] G. C. Corfield, Chem. Soc. Rev., 1(4), 523 (1972).
[2] C. G. Overberger and S. Ishida, J. Polym. Sci., B, 3, 789 (1965).
[3] C. G. Overberger, G. Montaudo, and S. Ishida, J. Polym. Sci., A-1, 7, 35 (1969).
[4] T. L. Cairns, U.S. Patent 2,541,152.
[5] C. Schuster and E. Gassenmeier, German Patent 911,017.
[6] A. Crawshaw and A. G. Jones, J. Macromol. Sci.—Chem., A5, 51 (1971).
[7] A. G. Jones, Ph.D. Dissertation, Council for National Academic Awards (Great Britain), 1968.
[8] R. Hart, Bull. Soc. Chim. Belg., 66, 229 (1957).
[9] M. S. Kharasch, S. S. Kane, and H. C. Brown, J. Amer. Chem. Soc., 64, 1621 (1942).

[10] D. H. Lorentz in Encyclopedia of Polymer Science and Technology, Vol. 14, Wiley-Interscience, New York, 1971, p. 244.
[11] W. A. Schroeder, P. E. Wilcox, K. N. Trueblood, and A. O. Dekker, Anal. Chem., 23, 1740 (1951).
[12] R. C. Schultz and H. Hartman, Monatsh. Chem., 92, 307 (1961).
[13] P. Ganis, G. Avitabile, E. Benedetti, C. Pedone, and M. Goodman, Proc. Nat. Acad. Sci., 67, 426 (1970).
[14] E. J. Stamhuis, W. Mass, and H. Wynberg, J. Org. Chem., 30, 2160 (1965).
[15] J. Szmuszkovicz, Advan. Org. Chem., 4, 1 (1963).
[16] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, J. Amer. Chem. Soc., 85, 207 (1963).
[17] S. K. Malhotra, in Enamines (A. G. Cook, ed.), Dekker, New York, 1969, Chap. 1, p. 38.
[18] S. F. Dyke, The Chemistry of Enamines, Cambridge Univ. Press, Cambridge, 1973, p. 10.
[19] R. Greenhaigh and W. A. Weinberger, Can. J. Chem., 43, 3340 (1965).
[20] J. G. Roberts, J. Chem. Soc., 1964, 176.
[21] H. K. Hall Jr. and R. Zbinden, J. Amer. Chem. Soc., 80, 6428 (1958).
[22] A. R. Katritsky and A. P. Ambler, in Physical Methods in Heterocyclic Chemistry, Vol. 2 (A. R. Katritsky, ed.), Academic, New York, 1963.
[23] R. Mecke and F. Langenbucher, Infrared Spectra of Selected Chemical Compounds, Heyden, London, 1965, No. 430.
[24] F. Cortese, Org. Syn., Coll. Vol. II, 91 (1943).
[25] R. C. O'Gee and H. M. Woodburn, J. Amer. Chem. Soc., 73, 1370 (1951).
[26] H. E. Newman, Chem. Ber., 24, 2192 (1891).
[27] A. N. Smirov and I. F. Spasskava, Zh. Obshch. Khim., 35(1), 178 (1965).
[28] O. J. Scherer and M. Schmidt, Chem. Ber., 98, 2243 (1965).