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A. Crawshaw^{ab}; A. G. Jones^{ac}

^a Department of Chemistry and Biology Liverpool, Regional College of Technology, Liverpool, England

^b Department of Chemistry, Sheffield Polytechnic, Sheffield, England ^c Department of Chemistry, Widnes Technical College, Widnes, Lanes, England

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The Preparation and Polymerization of N, N'-Divinylureas *

A. CRAWSHAW† and A. G. JONES‡

*Department of Chemistry and Biology
Liverpool Regional College of Technology
Liverpool 3, England*

SUMMARY

A new synthetic route to N,N'-disubstituted-N,N'-divinylureas is described. The method involves the preparation of the disodium salts of N,N'-disubstituted ureas, their conversion to the corresponding di-(β -dimethylaminoethyl) derivatives and the application of the Cope or the Hofmann reaction to these. 1,3-Divinylimidazolid-2-one (Va), 1,3-divinylhexahydropyrimid-2-one (Vb), and N,N'-diphenyl-N,N'-divinylurea (Vc) have been prepared by this route. The two cyclic N,N'-divinylureas (Va and Vb) were polymerized, using a radical initiator, to heavily cross-linked polymers containing a significant proportion of residual N-vinyl groups. There is no apparent evidence from IR spectra for the bicyclic units which would be present if any cyclopolymerization had occurred. The diphenyl compound (Vc) could not be polymerized under a variety of conditions and initiators. An explanation is suggested for the inability of Va and Vb to cyclopolymerize.

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†Present address: Department of Chemistry, Sheffield Polytechnic, Sheffield S1 1WB, England.

‡Present address: Department of Chemistry, Widnes Technical College, Widnes, Lancs., England.

INTRODUCTION

Our earlier attempts [1] to prepare N,N' -divinylurea by a variety of elimination reactions on appropriate precursors led to a range of products but not to the required N,N' -divinylurea. In general, the more "acidic" hydrogen atoms on the nitrogen atoms of the urea grouping were removed rather than those on the carbon atoms in β -positions to the functional groups.

Soon after the publication of these results, Overberger and Ishida [2] reported the preparation of N,N' -divinylurea and its polymerization, with a radical initiator, to "largely insoluble polymers" whose IR spectra "indicated the dominant cyclic structure with some pendent vinyl groups." In a recent paper [3], these authors suggest that further IR and NMR studies do not support the presence of cyclized units in these polymers although there were some indications that poly(N,N' -divinylurea) from photopolymerization reactions possessed, partially, cyclic structures.

Another approach to the synthesis of N,N' -divinylurea, investigated by ourselves and by Overberger et al. [3], was the reaction of vinyl isocyanate with water in a 2:1 molar ratio (Fig. 1). The reaction was exothermic, carbon dioxide was evolved, and an alkaline solution formed. The products, however, were white polymeric solids, completely insoluble, and decomposing at about 200°C. The IR spectrum showed the presence of $-NH-$ ($3,300\text{ cm}^{-1}$), acyclic carbonyl (1640 cm^{-1}), $-CO.NH-$ ($1530-1550, 1245\text{ cm}^{-1}$), residual $-CH=CH_2$ ($980, 850\text{ cm}^{-1}$), and the absence of residual isocyanato groups. Professor Overberger kindly compared the spectrum of our polymer with that of the poly(N,N' -divinylurea) prepared from N,N' -divinylurea by Dr. Ishida. Although there were a few minor differences in the two spectra, it is a reasonable conclusion that the vinyl isocyanate-water product is a low molecular weight poly(N,N' -divinylurea). Presumably the above reaction did produce N,N' -divinylurea which then polymerized under the reaction conditions.

RESULTS AND DISCUSSIONS

By starting from N,N' -disubstituted ureas (I), rather than from urea itself, the use of elimination reactions on suitable precursors should provide a route to N,N' -divinylureas (V). Three N,N' -divinylureas of this type have been prepared via the Cope and/or the Hofmann reaction, as shown (Fig. 2). This route appears to provide a general method for the synthesis of N,N' -disubstituted- N,N' -divinylureas.

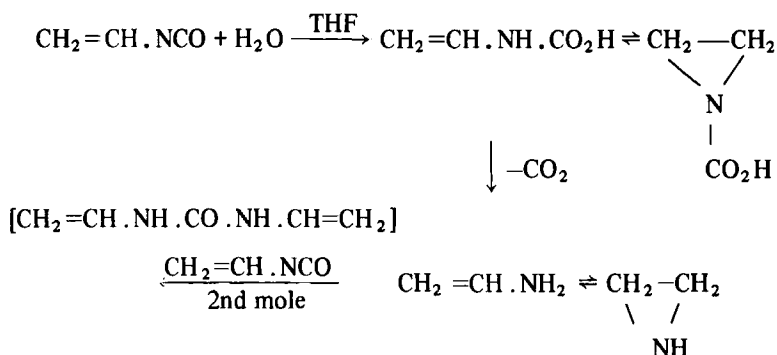


Fig. 1. Attempted synthesis of *N,N'*-divinylurea.

The preparation of 1,3-divinylimidazolid-2-one (Va) by a direct vinylation reaction on Ia using acetylene and a basic catalyst under pressure has been described in the patent literature [4, 5]. One of the patents [4] reports a radical-initiated polymerization of this product to an insoluble, cross-linked polymer.

The disodium salts of the *N,N'*-disubstituted ureas (I) were prepared using sodium hydride in *N,N*-dimethylformamide and reacted in situ with β -dimethylaminoethyl chloride to give the ditertiary amines (II). Considerable decomposition occurred during attempts to vacuum distil the ditertiary amines so that, in general, they were converted directly to the diquaternary ammonium iodide derivatives (III) or the di-N-oxides (IV) without further purification. The diiodides (III) were white, crystalline compounds which provided the confirmatory analytical and spectral data. The corresponding hydroxides, obtained as viscous oils, were decomposed by heating, either alone or in cyclohexanol solution, at temperatures from 87° to 155°C. The *N,N'*-divinylureas (Va, Vb, Vc) were obtained in high yield as white, crystalline compounds and appropriate analytical data confirmed their structures.

For example, 1,3-divinylhexahydropyrimid-2-one (Vb) gave a correct elemental analysis; strong absorption bands in the IR spectrum at 978 and 837 cm^{-1} ($\text{N}-\text{CH}=\text{CH}_2$), 1630 cm^{-1} ($\text{C}=\text{C}$), 1660 cm^{-1} ($\text{C}=\text{O}$), and 1260 cm^{-1} (Amide III); a mass spectrum confirming the molecular formula as $\text{C}_8\text{H}_{12}\text{N}_2\text{O}$ and an NMR spectrum showing an ABX spin system with four regions of absorption, at 2.2-2.8 τ ($\text{N}-\underline{\text{C}}\text{H}=\text{CH}_2$), 5.5-5.9 τ ($\text{N}-\text{CH}=\text{CH}_2$), 6.4-6.8 τ (protons at C_4 and C_6), and 7.6-8.1 τ (protons at C_5) of relative areas 1:2:2:1, respectively.

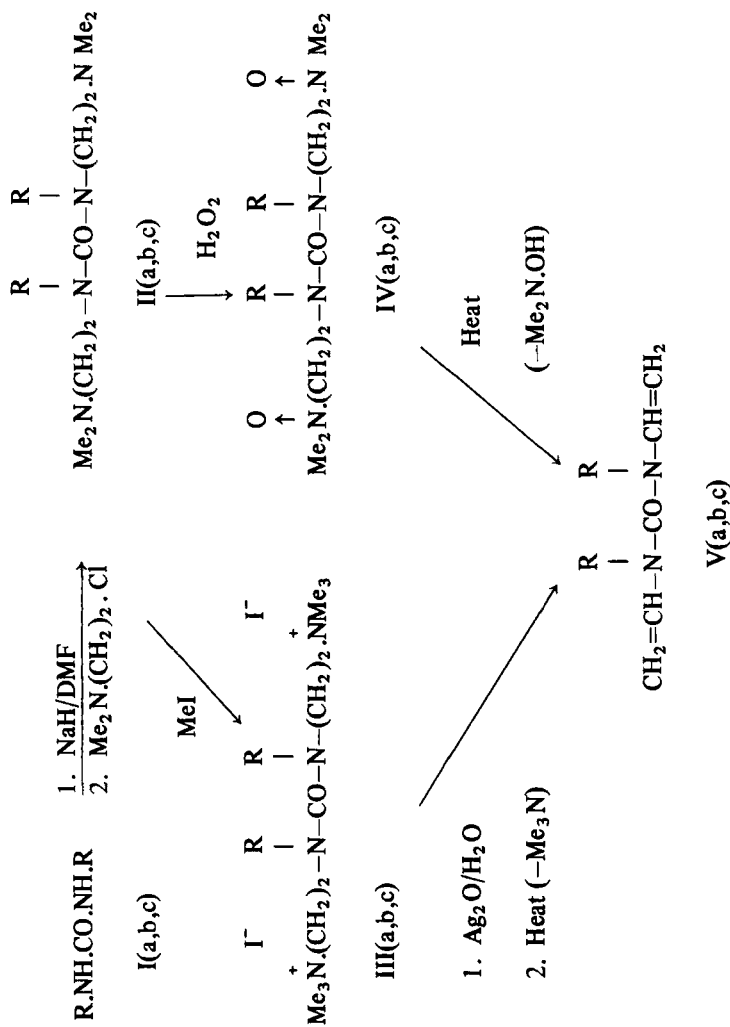


Fig. 2. Preparation of N,N'-divinylureas via the Cope and Hofmann reactions.

The polymerization of the two cyclic *N,N'*-divinylureas (Va, Vb) occurred very readily with azodiisobutyronitrile as initiator in *N,N*-dimethylformamide solution. The polymers were obtained initially in gelatinous form, separating either spontaneously from the polymerization mixture or on the addition of the mixture to ether. By centrifuging and vacuum drying, the polymers were converted to white, granular material. With both monomers, almost quantitative conversion to polymer occurred; for example, on polymerizing a 20% solution of monomer at 70°C with 2 mole % (relative to monomer) of initiator for about 1 hr.

The polymers were completely insoluble in a wide range of solvents and showed no signs of melting up to 335°C, the limit of the heating block. They appear, therefore, to have heavily cross-linked structures.

The physical nature of these polymers has limited their structural analysis by spectroscopic procedures. The IR spectra show that the polymers from both monomers contain a significant proportion of residual *N*-vinyl groups. The position of the absorption band for the carbonyl group (Amide II band) could be of particular value in a structural diagnosis, since it is known that this group absorbs at different wavelengths in various acyclic and cyclic situations [6]. High resolution IR spectra of the polymers show multiple bands in the region of the carbonyl stretching frequency and it is not possible, from current literature information, to adequately relate these to the various possible structural environments of the carbonyl groups in these polymers. There is no apparent evidence for the presence of carbonyl groups in bicyclic structures, which would be formed if cyclopolymerization had occurred. It would be valuable to have additional IR data from a number of model bicyclic compounds and, in particular, to obtain soluble polymers from these monomers so that further spectroscopic techniques could be applied. However, from the heavily cross-linked nature of these polymers and the significant proportion of residual *N*-vinyl groups it appears that little, if any, cyclopolymerization can have occurred.

The *N,N'*-diphenyl-*N,N'*-divinylurea (Vc) could not be polymerized under a variety of conditions and initiators, the latter including azodiisobutyronitrile, boron trifluoride-etherate, and lithium- and sodiumnaphthalene.

For cyclopolymerization to occur, the two vinyl groups (in Va and Vb) would need to move into the necessary positions for the intramolecular step, either before or during the involvement of the particular molecule in the polymerization. In Vb this would mean a "cis di-axial" arrangement of the vinyl groups, which is possible, hypothetically at least, either by ring inversion or by inversion at the nitrogen atoms. In Va it would mean a cis arrangement of the vinyl groups, which could be achieved by inversion

at the nitrogen atoms. The situation is analogous to that of *cis*-1,3-divinylcyclohexane and *cis*-1,3-divinylcyclopentane, both of which have been cyclopolymerized [7]. In Vb and Va, if such inversions occurred easily and rapidly relative to the polymerization process, then predominant cyclopolymerization would be expected.

Such an arrangement of the vinyl groups would move them out of the plane of the —N—CO—N— grouping, a process presumably involving a considerable loss of resonance energy. Models of these molecules would suggest a very stable coplanar arrangement by overlap of p_z orbitals throughout the $\text{CH}_2=\text{CH—N—CO—N—CH}=\text{CH}_2$ system (Fig. 3), assuming sp^2 hybridization for the nitrogen atoms with each having a pair of electrons in the $2p_z$ orbital. The retention of such a planar arrangement would lead to intermolecular propagation and the cross-linked polymers obtained experimentally.

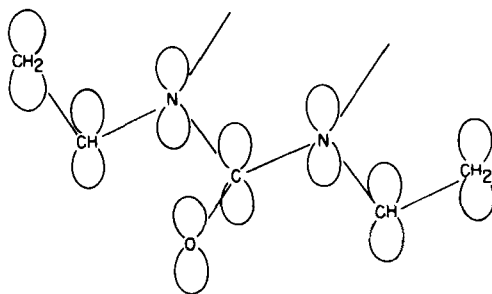


Fig. 3. Model of the $\text{CH}_2=\text{CH—N—CO—N—CH}=\text{CH}_2$ system.

EXPERIMENTAL

IR spectra were recorded as liquid films or as potassium bromide disks using a Perkin-Elmer Infracord 137. The recorded spectra were calibrated against a polystyrene film absorption peak at 1603 cm^{-1} . Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were determined at normal temperatures for deuteriochloroform or carbon tetrachloride solutions, containing tetramethylsilane ($\tau = 10$) as internal reference standard, on a 60 Mc Perkin Elmer spectrometer. Mass spectra were recorded on the A.E.I. M.S.9 spectrometer.

1,3-Di-(β -dimethylaminoethyl)imidazolid-2-one (IIa). Imidazolid-2-one

(15 g, 0.17 mole) was dissolved, with stirring, in anhydrous N,N-dimethylformamide (280 ml) in a 1-liter flask fitted with an efficient reflux condenser. Sodium hydride (20 g), as a 50% dispersion in oil, was added and the mixture stirred vigorously. β -Dimethylaminoethyl chloride (39.6 g, 0.37 mole) dissolved in anhydrous N,N-dimethylformamide (40 ml) was added and the temperature of the mixture was slowly raised to 120° over a period of 2 hr. This temperature was maintained for a further 14 hr and the reaction mixture, after cooling, was then poured into water, the whole extracted with chloroform, and the extract dried over magnesium sulfate. Removal of the chloroform under reduced pressure gave 1,3-di-(β -dimethylaminoethyl)imidazolid-2-one (IIa) as a red liquid (36.6 g, 92% yield), showing absorption bands in the IR spectrum at 2800 cm^{-1} (NMe₂), 1680-1685 cm^{-1} (C=O), and 1250 cm^{-1} (Amide III).

Dimethiodide of IIa. IIa (22.8 g, 0.1 mole) was dissolved in anhydrous ether (150 ml) and methyl iodide (28.4 g, 0.2 mole), dissolved in ether (40 ml), was added dropwise over 30 min. A white solid precipitated which was crystallized from absolute ethanol to give the dimethiodide of IIa (37.3 g, 73% yield) as white flakes, mp 280° with decomposition (found: C, 30.26; H, 5.87; N, 10.53; C₁₃H₃₀I₂N₄O requires C, 30.47; H, 5.90; N, 10.39%).

1,3-Divinylimidazolid-2-one (Va) from the Dimethiodide. The dimethiodide of IIa (60 g, 0.117 mole) was dissolved in water (120 ml), silver oxide (30 g, 0.129 mole) was added, and the mixture stirred at room temperature until the supernatant liquid was free of iodide ions. Filtration through hardened filter paper and concentration of the aqueous filtrate in vacuo gave the corresponding dihydroxide as a colorless syrup. The syrup was decomposed under nitrogen at 100° and 13 mm pressure in an apparatus fitted with a nitrogen "bleed" and connected through a short-path condenser and receiver, and cold traps at -70°, to an oil pump. The solid product collected in the first (room temperature) receiver was recrystallized from methanol-water to give 1,3-divinylimidazolid-2-one (Va) as white flakes (10.8 g, 67% yield), mp 65.5° (found: C, 60.63; H, 7.20; N, 19.86; calc for C₇H₁₀N₂O: C, 60.85; H, 7.30; N, 20.28%). IR absorption bands were at 1715-1725 cm^{-1} (C=O), 1635 cm^{-1} (C=C), 1270-1280 cm^{-1} (Amide III), and 983 and 842 cm^{-1} (N-CH=CH₂). NMR spectrum showed a series of peaks at 2.6-3.2 and 5.6-6.1 τ , and a singlet at 6.3-6.5 τ , assigned to $-\underline{\text{C}}\text{H}=\text{CH}_2$, $-\text{CH}=\underline{\text{C}}\text{H}_2$, and $-\underline{\text{C}}\text{H}_2-\underline{\text{C}}\text{H}_2-$ hydrogens, respectively. The integrated peak areas ratio for sp²:sp³ hydrogens is 6:4 (theoretical 6:4).

The condensate in the cold traps was confirmed as trimethylamine through its hydrochloride (mp and mixed mp 287° , with decomposition).

Di-N-oxide of IIa. A solution of IIa (13.8 g, 60 mmole) in methanol (20 ml) was cooled to 0° and 30% hydrogen peroxide solution (40.8 g, 0.36 mole) was added over a period of 30 min. After allowing the mixture to warm up to room temperature and stand for 20 hr, powdered manganese dioxide (0.5 g) was added and the mixture stirred for 21 hr. After this period the supernatant liquid gave no coloration with starch-iodide paper. The mixture was filtered through hardened filter paper and the water-methanol removed from the filtrate at $30-40^{\circ}$ and 15-20 mm pressure to give the di-N-oxide (12 g) as a viscous syrup.

1,3-Divinylimidazolid-2-one (Va) from the Di-N-oxide. The above syrup (12 g) was decomposed at 130° under nitrogen at 4.7 mm pressure in an apparatus similar to that described previously. At 166° a colorless liquid was collected and crystallized in the room-temperature receiver. Recrystallization (methanol-water) afforded 1,3-divinylimidazolid-2-one (Va) as white plates (1.67 g, 20% yield) with mp and mixed mp 65.5° and identical IR spectrum to the sample previously prepared. The condensate in the cold traps was confirmed as dimethylhydroxylamine through its hydrochloride (mp 107° and correct elemental analysis).

Poly(1,3-divinylimidazolid-2-one). A typical polymerization was carried out as follows: 1,3-divinylimidazolid-2-one (2 g, 14.5 mmole) was dissolved in anhydrous N,N-dimethylformamide (8 g) in a Pyrex tube and azodiisobutyronitrile (0.047 g, 0.29 mmole) added. The mixture was swept with dry nitrogen, sealed, and agitated in a thermostat bath at 70° for $1\frac{1}{2}$ hr. Residual solvent was removed in vacuo, and the resultant white solid ground to powder prior to continuous extraction with methanol. The unextracted white powder was poly(1,3-divinylimidazolid-2-one), (1.85 g, 93% yield), mp $> 335^{\circ}$, completely insoluble in a wide range of solvents, and with IR absorption bands at $1690-1710\text{ cm}^{-1}$ (C=O), 1270 cm^{-1} (Amide III), 1635 cm^{-1} (residual C=C), and 980 and 830 cm^{-1} (residual N-CH=CH₂). Other polymerization experiments varied the conditions and the component ratios as shown in Table 1. Similar white polymers were obtained, with identical physical and spectroscopic characteristics to the one described above.

1,3-Di-(β -dimethylaminoethyl)hexahydropyrimid-2-one (IIb). Ib (17.4 g,

Table 1

Monomer (mmole)	Solvent (g)	Initiator (mmole)	Concentration		Temp (°C)	Time (hr)
			Monomer in solvent(% w/w)	Initiator to monomer(mole %)		
3.9	26.3	0.07	2	2	70	3 ^a
3.6	24.5	0.07	2	2	70	22
3.6	10.0	0.07	4.75	2	70	1.5

^aPolymer precipitated by addition of ether.

0.17 mole) was stirred with anhydrous N,N-dimethylformamide (280 ml) in a 1-liter flask fitted with an efficient reflux condenser. Sodium hydride (20 g) was added as a 50% dispersion in oil, followed by β -dimethylaminoethyl chloride (39.6 g, 0.37 mole) dissolved in anhydrous N,N-dimethylformamide (100 ml). The mixture was stirred and slowly warmed to 60° when the reaction became vigorously exothermic. After the reaction had subsided, the mixture was kept at 95° for 5 hr. The mixture, after cooling, was then poured into excess dilute hydrochloric acid solution and the whole extracted with chloroform to remove the oil introduced with the sodium hydride. The aqueous layer was made alkaline with sodium hydroxide solution and continuously extracted with chloroform. The extract was dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure to give 1,3-di-(β -dimethylaminoethyl) hexahydropyrimid-2-one (IIb) as a red liquid (30.6 g, 73% yield). IR absorption peaks at 2800 cm^{-1} ($-\text{NMe}_2$), 1640-1660 cm^{-1} (C=O), and 1295 cm^{-1} (Amide III).

Dimethiodide of IIb. IIb (27.2 g, 0.11 mole) was dissolved, with stirring, in anhydrous ether (300 ml), and methyl iodide (31.9 g, 0.225 mole) in ether (50 ml) was added dropwise over 30 min. The resultant white precipitate was collected and recrystallised from methanol to give the dimethiodide of IIb (38 g, 64% yield), mp 248-252° with decomposition (found: C, 31.66; H, 6.17; N, 10.35; $\text{C}_{14}\text{H}_{32}\text{I}_2\text{N}_4\text{O}$ requires C, 31.95; H, 6.13; N, 10.65%).

1,3-Divinylhexahydropyrimid-2-one (Vb). The dimethiodide of IIb (21.1 g, 0.04 mole) was dissolved in methanol (100 ml), silver oxide (10 g, 0.043 mole) was added, and the mixture stirred at room temperature until the supernatant liquid was free of iodide ions. The mixture was filtered through hardened filter

paper and the filtrate concentrated in vacuo to give the corresponding dihydroxide as a brown oil. The oil was decomposed at 87° in vacuo to give a brown liquid residue which crystallized on cooling. Recrystallization from petroleum ether ($40-60^{\circ}$) gave 1,3-divinylhexahydropyrimid-2-one (Vb) as white flakes (5.1 g, 84% yield), mp $65-6^{\circ}$ (found: C, 63.17; H, 7.79; N, 18.69; $C_8H_{12}N_2O$ requires C, 63.13; H, 7.95; N, 18.41%). IR, NMR, and mass spectroscopic data for Vb are given earlier. The condensate in the cold trap was identified as trimethylamine, as already described for Va.

Poly(1,3-divinylhexahydropyrimid-2-one). A typical polymerization was carried out as follows: Vb (0.5 g, 3.3 mmole) in anhydrous N,N-dimethylformamide (2 g) and azodiisobutyronitrile (0.0108 g, 0.07 mole) were sealed in a Pyrex tube, under nitrogen, and agitated at 70° for $\frac{1}{2}$ hr. The gelatinous solid product was collected by centrifuging, dried under vacuum, and finally ground to a white powder. The solid remaining after continuous extraction with methanol was poly(1,3-divinylhexahydropyrimid-2-one), mp $>335^{\circ}$, and insoluble in a wide range of solvents. The IR spectrum showed the same absorption peaks as the monomer (already given) but with the peaks arising from the vinyl groups being severely reduced in intensity. A broad absorption band appeared at $2880-2940\text{ cm}^{-1}$ (CH_2) in the polymer spectrum.

N,N'-Di-(β -dimethylaminoethyl)-N,N'-diphenylurea (IIc). Ic (37 g, 0.17 mole) in anhydrous N,N-dimethylformamide (250 ml), sodium hydride (20 g) as dispersion, and β -dimethylaminoethyl chloride (39.6 g, 0.37 mole) in anhydrous N,N-dimethylformamide (150 ml) were reacted together at 120° for 16 hr. The cooled mixture was poured into water and a white solid which precipitated was identified as 1,3-diphenylimidazolid-2-one (5.1 g, 12% yield based on Ic), mp $218-219^{\circ}$ (lit., 216°) (from 95% ethanol), and giving a correct elemental analysis. The aqueous solution, after filtration, was continuously extracted with ether, and the extract, on removal of the ether, gave a reddish liquid which was alkaline to litmus. The liquid was poured into excess dilute hydrochloric acid solution and the whole continuously extracted with ether. The ether extract contained unchanged N,N'-diphenylurea (4.2 g, 11%). The remaining aqueous solution was made alkaline with sodium hydroxide solution and extracted with ether. The extract was treated in the usual way to give N,N'-di-(β -dimethylaminoethyl)-N,N'-diphenylurea (IIc) as a red liquid (47.2 g, 76%). Absorption bands in the IR absorption spectrum were at $2740-2820\text{ cm}^{-1}$ ($-NMe_2$), $1630-1655\text{ cm}^{-1}$ ($C=O$), and 694, 754, 1498, and 1598 cm^{-1} (monosubstituted benzene).

Dimethiodide of IIc. IIc (37.2 g, 0.105 mole) in absolute alcohol (350 ml) was treated, dropwise over 30 min, with a solution of methyl iodide (30.2 g, 0.213 mole) in absolute alcohol (50 ml), the mixture being maintained at 50°. The white precipitate formed was recrystallized from methanol to give the dimethiodide of IIc as colorless needles of the monohydrate (56.9 g, 85% yield), mp 275-277° with decomposition (found: C, 42.07; H, 5.63; N, 8.16; C₂₃H₃₆I₂N₄O.H₂O requires C, 42.07; H, 5.83; N, 8.54%).

N,N'-Diphenyl-N,N'-divinylurea (Vc). The dimethiodide of IIc (18 g, 28 mmole) in methanol (200 ml) was treated with silver oxide (10 g) and the mixture stirred and kept at 40° until the supernatant liquid was free of iodide ions. After filtration, a colorless, alkaline solution of the corresponding dihydroxide was obtained. Cyclohexanol (150 ml) was added to this solution, the methanol present removed by distillation, and the residual mixture heated at 155° for 20 hr, during which time trimethylamine (identified as its hydrochloride) was continuously evolved. The cyclohexanol was removed under reduced pressure to yield a crystalline solid, recrystallized from petroleum ether (60-80°) to give N,N'-diphenyl-N,N'-divinylurea (Vc) as white needles (6.7 g, 90% yield), mp 116° (found: C, 77.50; H, 6.04; N, 10.79; C₁₇H₁₆N₂O requires C, 77.25; H, 6.10; N, 10.60%). Peaks in the IR absorption spectrum were at 1660 cm⁻¹ (C=O), 1630 cm⁻¹ (C=C), and 697, 750, 1494 and 1595 cm⁻¹ (monosubstituted benzene). The NMR spectrum shows series of peaks at 2.6-3.1, 3.3-3.6, and 5.7-6.4 τ , assigned to $-\underline{\text{C}}\text{H}=\text{CH}_2$ and meta- and para-protons, orthoprotons, and $-\text{C}\underline{\text{H}}_2$ protons, respectively. The integrated peak areas were 8:4:4 (theoretical 8:4:4).

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