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Jones and Mason claimed a number of years ago (1) that rearrangement of *cis*-olefinic acyl azides gave *trans*-olefinic isocyanates. However, several other workers have found that rearrangement of an acyl azide group attached to an optically active carbon gives configurationally identical products, a discovery which apparently conflicts with Jones and Mason's findings. We have reexamined the rearrangement of *cis*-cotonyl azide with stringent checks at each reaction step and found perfect retention of geometry in the product. Details of this finding are discussed.

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Introduction

The Curtius rearrangement of an acyl azide to an isocyanate with loss of nitrogen has, with saturated aliphatic acyl azides, no special stereochemical involvement. However, with the rearrangement of unsymmetrical olefinic acyl azides, two possible courses are open. A number of years ago, Jones and Mason (1) reported that the rearrangement of *cis* olefinic acyl azides, at least for *cis*-cinnamyl (3b, $R = C_6H_5$) and *cis*crotonyl (3b, $R = CH_3$) azides, gave *trans*olefinic isocyanates (4a), the same as those obtained from *trans*-olefinic acyl azides. This finding has been mentioned with reservations by review authors (2).

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While trying to prepare *cis*-crotonyl chloride from *cis*-crotonic acid by the method of Jones and Mason (1, 3) we obtained largely the *trans* isomer (4). This experimental result has made us question their finding.

There are examples in the literature of optically active azido acyl compounds which have been rearranged to optically active isocyanates (5) (probably with retention of configuration (6)), of cis and trans cyclic 1,2-diacyl azides rearranged with retention of geometry (7), of retention of endo or exo configuration on rearrangement of the corresponding 2-azidoacyl norbornanes (8), and an example of an analogous cyclic 1,3-diacylazide rearrangement which was not stereospecific (9). Consequently, we felt that the question of the stereospecificity of the rearrangement of olefinic acyl azides had not as yet been adequately answered and for us, use of the crotonyl azide as the starting point was the obvious choice.

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TABLE I

Nuclear magnetic resonance data for crotonyl azides and propenyl isocyanates*

Compound†	Double doublets CH ₃ —		Overlapping quartet pairs —CH—		Quartet pairs ==CHX	
	Shift	Coupling	Shift	Coupling	Shift	Coupling
cis-Crotonyl azide	2.85	$J_{ab} = 7.35$ $J_{ac} = 1.8$	6.50	$J_{ba} = 7.3$ $J_{bc} = 11.0$	5.75	$J_{ca} = 1.8$ $J_{cb} = 11.0$
trans-Crotonyl azide	1.91	$J_{ab} = 6.7$ $J_{ac} = 1.6$	7.10	$J_{ba} = 6.8$ $J_{bc} = 15.0$	5.83	$J_{ca} = 1.6$ $J_{cb} = 15.0$
cis-Propenyl isocyanate	1.68	$J_{ab} = 6.8$ $J_{ac} = 1.7$	5.23	$J_{ba} = 6.8 \ddagger J_{bc} = 7.2 \ddagger$	5.89	$J_{cs} = 1.7$ $J_{cb} = 7.2$
trans-Propenyl isocyanate	1.64	$J_{ab} = 6.2 \\ J_{ac} = 1.2$	5.50	$J_{bc} = 6.2$ $J_{bc} = 12.6$	5.69	$J_{ca} = 1.2 \\ J_{cb} = 12.6$

*In the formula CH₃—CH=CH-X; CH₃-,-CH=, and =CH-X are represented by a, b, and c respectively. †The solvent used was deuteriochloroform. ‡Resultant, a broad quintet.

Experimental

Trans-crotonyl chloride, containing about 2% of the cis isomer, was purchased from Eastman Organic Chemicals. The unambiguous preparation of cis-crotonyl chloride has been described previously (4). Melting points and boiling points are not corrected. Infrared (i.r.) spectra were obtained on a Perkin-Elmer model 337 grating spectrophotometer using thin films between rock salt plates.

Azide Preparations and Decompositions trans-Crotonyl Azide

trans-Crotonyl chloride (104 g, 1 mole) was added to a well-stirred slurry of dry, finely-ground sodium azide (130 g, 2 moles) in dry ether (400 ml). Stirring, with protection from atmospheric moisture, was continued for 64 h while thermostatting in a water bath at 25 °C. The sodium chloride and unreacted sodium azide were then filtered off, and the ether was removed from the filtrate by raising the bath temperature to 30 °C and applying aspirator vacuum. The residual yellow oil (95.5 g) contained a substantial amount of the azide (i.r. maximum at 2148 cm⁻¹) and a lesser amount of the isocyanate (i.r. maximum at 2265 cm⁻¹) in addition to some (about 30%) unreacted acid chloride.

Azide preparations which were carried out in an aqueous medium were very much quicker and gave better yields. *trans*-Crotonyl chloride (52 g, 0.5 mole) in acetone (25 ml) was added dropwise over 15 min to a well-stirred solution of sodium azide (37 g, 0.5 mole) in water (100 ml) at room temperature. After the first 2 min of addition the remainder of the reaction was carried out with cooling in an ice-water bath, and stirring was continued for a further 5 min after completion of the addition. The organic phase was separated and dried (MgSO₄) yielding 47 g (85% yield) of pale-yellow oil. By nuclear magnetic resonance (n.m.r.) and i.r. this was found to be essentially *trans*-crotonyl azide free of isocyanate or acid chloride, and containing only a trace of acetone The azide effervesced very slowly at room temperature.

trans-Propenyl Isocyanate

Azide prepared in ether could not be separated from

isocyanate by cold (25 °C bath) distillation so the crude mixture obtained from the azide preparation was decomposed without isolation. The mixture (92 g) diluted with dry *m*-xylene (125 ml), was heated under a reflux condenser on a boiling water bath for 1 h when decomposition was complete (no azide band in i.r.). This solution was distilled through a 30 cm high Widmer column to recover the isocyanate which was collected in two fractions: 11 4 g (b.p. 80-84 °C) and 12.0 g (b.p. 84-101 °C); followed by 30 g (b.p. 101-130 °C; most at 126 °C) of recovered trans-crotonyl chloride. Redistillation of the first two fractions through the same column gave 10.1 g of trans-propenyl isocyanate (b.p. 78-82 °C, n.m.r. in Table I) containing a trace of cis, and 10.8 g of slightly less pure material. They were colorless, highly lachrymatory mobile oils. The yield based on crotonyl chloride consumed was 35%

When purer azide (prepared by aqueous method) was decomposed as described above better yields of isocyanate were expected. However, while isocyanate was being distilled over, white solids (probably polymeric) formed in the still pot and only 10 g of monomeric isocyanate could be recovered from 45–50 g of azide, the same overall yield as previously.

trans-Propenyl Urea

Dry ammonia gas was played onto the surface of a stirred, ice-cold solution of *trans*-propenyl isocyanate (1.2 g) in dry ether (25 ml) until precipitation ceased. The white solid (1.2 g) was removed by filtration and dried, m.p. 106-111 °C. Two recrystallizations of this precipitate from ethyl acetate – chloroform (1:7 by volume) with a minimum of heating (very susceptible to polymerization) sharpened but simultaneously lowered the melting point to 99-101 °C (lit. (1) m.p. 122 °C), after final drying at 0.01 mm pressure for 8 h.

Anal. Calcd. for $C_4H_8N_2O$: C, 48.0; H, 8.1; N, 28.0. Found: C, 47.4, 47.2; H, 8.2, 8.1; N, 27.3, 27.4.

cis-Crotonyl Azide

cis-Crotonyl chloride (51 g, 0.49 mole) was added to a well-stirred slurry of dry finely-ground sodium azide (52 g, 0.80 mole) in dry ether (250 ml) kept in a thermostat bath at +9 °C. After stirring for 24 h an aliquot was

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TABLE II						
Nuclear magnetic resonance data for propenyl ureas*						

	trans-Propenyl urea			cis-Propenyl urea		
Assignment†	Shift	Multiplicity	Coupling	Shift	Multiplicity	Coupling
CH ₃ —	1.58	Double doublet	$J_{ab} = 6.8$ $J_{ac} = 1.6$	1.53	Double doublet	$J_{ab} = 7.1$ $J_{ac} = 1.6$
-CH=	4.80	Overlapping quartet pair	$J_{ba} = 6.8$ $J_{bc} = 14.4$	4.57	Overlapping quartet pair	$J_{ba} = 7.1$ $J_{bc} = 9.0$
=CH-	6.43	Three multi- plet groups	complex	6.44	Two multi- plet groups	complex
NH	8.12	Broad doublet	$J_{dc} = 10.5$	7.95	Broad doublet	$J_{dz} = 11.1$
—NH₂	3.57	Singlet		3.64	Singlet	

*The solvent used was dimethylsulfoxide-d₆ †In the formula CH₃—CH=CH—NH—CO—NH₂; CH₃—, —CH=, =CH—, —NH—, and —NH₂ are represented by a, b, c, d, and e respectively.

withdrawn, the ether was evaporated. The residual oil contained only a very slight trace of azide and no isocyanate (by i.r.). The bath temperature was raised to 31 °C and stirring continued for a further 14 h when another aliquot was checked and found to be as before. The temperature was then raised to 42 °C and stirring continued for 24 h more with no progress evident. The sodium azide was then filtered off and 35 g of cis-crotonyl chloride (now containing about 5% trans) were recovered by distillation at 20 mm. Attempted preparation of cis azide at 65 °C in diethyl triethylene glycol was as unpromising as the diethyl ether reaction.

Aqueous preparations were successful. 97% cis-Crotonyl chloride (52 g, 0.5 mole) in acetone (25 ml) at 0 °C was added over 15 min to a vigorously stirred solution of sodium azide (39g, 0.6 mole) in water (105 ml) kept at +4 to +7 °C in an ice-salt bath. Preparations where the reaction temperature was allowed to run as high as 15-20 °C gave significantly lower retention of cis geometry. Stirring was continued for 5 min after completion of the addition, and then the organic layer was separated, washed with ice-water (120 ml), and dried (MgSO₄) yielding 48 g of colorless oil. Infrared analysis indicated this material was predominantly azide though traces of isocyanate, the cis acid, and acetone were present. Nuclear magnetic resonance integrals established that 85% of the azide present was cis. After 17 h at 25 °C, 8% of a sample of azide had decomposed to isocyanate, but another sample kept one week at -24 °C showed no decomposition. A wash of 23.5 g of the crude azide with weak brine (2 \times 100 ml) at $-5\ ^\circ C$ and two dryings (Na₂SO₄) reduced the quantity of recovered azide to 10.2 g and simultaneously eliminated the acetone and the cis acid that were present.

cis-Propenyl Isocyanate

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Preliminary preparations showed that decomposition of cis-crotonyl azide at temperatures above 45-50 °C gave some concomitant isomerization of cis-isocvanate to the trans configuration. Also, it was found that temperatures below 40 °C were low enough to prevent significant decomposition of trans-crotonyl azide. Apart from preparative reactions three decompositions carried out in a thermostat bath at $33(\pm 0.1)$ °C and protected from atmospheric moisture, were carefully followed by n.m.r., after a rough preliminary run in ether. Three grams of about 85% cis-crotonyl azide were placed in each of three test tubes. To one was added ether (12 ml), another deuteriochloroform (12 ml), and a third was left without solvent. All three were placed in the thermostat and aliquots were withdrawn at intervals and analyzed by n.m.r.; the presence of ether did not interfere. The results of these runs are summarized in Table IV and Fig. 2.

cis-Propenyl Urea

The remainder of the cis-crotonyl azide decomposition in deuteriochloroform was diluted with ether (25 ml) and treated with ammonia in the same way as the corresponding *trans* isomer to yield 1.2 g of cream-colored crystals, m.p. 100-108 °C. One recrystallization brought the m.p. to 111-114 °C, mixture m.p. with once recrystallized trans 94-98 °C. After two recrystallizations the m.p. was 117-118 °C and the mixture m.p. with twice recrystallized trans 92-111 °C. Nuclear magnetic resonance also confirmed its dissimilarity from the trans isomer (see Table II)

Anal. Calcd. for C₄H₈N₂O: C, 48.0; H, 8.1; N, 28.0. Found: C, 46.7, 47.1; H, 8.2, 8.2; N, 27.5, 27.8.

Nuclear Magnetic Resonance Analyses

The n.m.r. data reported were obtained using a Varian A60 instrument fitted with a phase detector integrator, and a Hewlett-Packard wide range oscillator (model 200CD) for sweep width calibration. Monitoring the oscillator was an electronic counter of the same make (model 5212A). All spectra were run at room temperature and shifts are reported in p.p.m. from internal tetramethyl silane corrected for sweep width variations. Coupling constants were measured on appropriate portions of spectra expanded to 50 cycles sweep width, and are reported in c.p.s. Integrals were all consistent with the assignments indicated.

(a) Curtius Rearrangements

Determination of the proportions of cis- and transcrotonyl azides and cis- and trans-propenyl isocyanates was accomplished by integration of the respective methyl

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Nuclear magnetic resonance data for methyl propenyl ureas*

N,N-Dimethyl-N'-trans-N-Methyl-N'-transpropenyl urea (R = H)propenyl urea ($R = CH_3$) Assignment[†] Shift Multiplicity Coupling Shift Multiplicity Coupling $J_{ab} = 6.7$ $J_{ab} = 6.8$ CH₃-1.57 Double I.58 Double $J_{ac} = 1.6$ doublet $J_{ac} = 1.7$ doublet 4.80 $J_{ba} = 6.7$ 5.03 $J_{ba} = 6.8$ Overlapping Overlapping quartet pair $J_{bc} = 14.1$ quartet pair $J_{bc} = 14.0$ =CH---Complex, ranging over 27 c.p.s. 6.48 Three multi-Complex 6.57 plet groups 8.08 Broad Broad $J_{dc} = 10.0$ 8.25 $J_{cc} = 10.5$ doublet doublet $-N(CH_3)$ 2.59 Two over-Ambiguous 2.82 Singlet lapping doublets‡ R 5.93 Eight Signal probable too weak

*The solvent used was dimethylsulfoxide-d₆. †In the formula CH₃—CH=CH—NH—CO—N(CH₃)R; CH₃—, —CH=, =CH—, —NH—, —N(CH₃), and R are represented by a, b, c, d, e, and f respectively. ‡Three peaks visible, ratio 1:2:1, spacing 2.7 and 2.1 cycles.

resonances (see Table I). Isocyanate methyl identity was double checked by adding small portions of the geometrically opposite analogous isocyanate. The methyl integrals on spectra expanded to 50 or 100 cycles sweep width were then totalled, and the proportion of each compound found by dividing its integral by the total.

(b) Preparation of Model Compounds

The N-H, and NH₂ assignments in the n.m.r. spectra obtained for cis- and trans-propenyl ureas were not completely unequivocal but the n.m.r. spectra of a number of new propenyl ureas of greater substitution eliminated any doubt. Description of the preparations of these model compounds follows and the n.m.r. data obtained for them in dimethylsulfoxide- d_6 are given in Table III.

N,N-Dimethyl-N'-trans-propenyl urea-An ice-cold solution of dimethylamine (2.5 ml) in dry ether (8 ml) was added with stirring and protection from atmospheric moisture to a solution of *trans*-propenyl isocyanate (1.6 g) in ether (25 ml). The white precipitate formed was filtered off, washed with a small portion of chilled ether, and dried yielding 1.8 g white crystals m.p. 142-149 °C. Recrystallization, once from ethyl acetate and once from acetone yielded 0.3 g of feathery plates m.p. 144–148 °C. Anal. Calcd. for $C_6H_{12}N_2O$: C, 56.2; H, 9.4; N, 21.9.

Found: C, 56.3; H, 9.9; N, 21.9, 21.7.

N-Methyl-N'-trans-propenyl urea-Using the method of the preceding preparation on trans-propenyl isocyanate (0.6 g) and adding gaseous methylamine above the solution yielded a precipitate which went back into solution on addition of further methylamine. Leaving the solution overnight with protection from atmospheric moisture yielded 0.49 g of rosettes of crystals m.p. 112-123 °C which were used as such.

Anal. Calcd. for C₅H₁₀N₂O: C, 52.6; H, 8.8; N, 24.5. Found: C, 52.6, 52.6; H, 9.0, 9.3; N, 24.5, 24.4.

N,N-Dimethyl-N'-cis-propenyl urea-Dimethylamine (4.5 ml) in ether (10 ml) was added in the same way as the analogous trans derivative, to cis-propenyl isocyanate obtained from the decomposition of 2.9 g of cis-crotonyl azide. The first crop of crystals (0.4 g) was rapidly made useless by deliquescense, but a second crop, (0.4 g) obtained by cooling the mother liquor to -22 °C, melted at 60--65 °C (sealed tube) and this was used for analysis.

Anal. Calcd. for C₆H₁₂N₂O: C, 56.2; H, 9.4; N, 21.9. Found: C, 56.5, 56.1; H, 9.7, 10.0; N, 22.0, 21.8.

(c) Study of D_2O Exchange with the Propenyl Ureas

The D₂O exchange experiments were carried out with cis- and trans-propenyl ureas with the same effects being observed with each. Initially spectra were run in dimethylsulfoxide-d₆ alone. Then gradually increasing amounts of D₂O were added to the DMSO solution with new spectra run each time. The changes observed for cis-propenyl urea are described and discussed later with our conclusions.

Results and Discussion

The sequence of reactions starting with transcrotonic acid through to trans-propenyl isocyanate was carried out straightforwardly by us according to the methods of Jones and Mason (1, 3) and each stage was carefully followed by nuclear magnetic resonance (n.m.r.) and infrared (i.r.) spectroscopy.

In this work the strongest n.m.r. signal in the spectra of all four compounds primarily involved in this series, the cis- and trans-crotonyl azides and cis- and trans-propenyl isocyanates, was that

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of the methyl group of the four compounds. Very conveniently for the purposes of this work nearly all of the double doublets representing the methyls of these four compounds were sufficiently well separated from each other to be used for the analysis of mixtures (Fig. 1 and Table I). While there was an overlap of one of the peaks in the *cis*-propenyl isocyanate methyl pattern with one for the methyl of trans-propenyl isocyanate, it was possible to use satisfactorily the remaining three unencumbered bands of each of the two compounds. This permitted easy direct determination of the proportions of each of the components present in aliquots removed from the main reaction solution, with minimal disturbance of conditions (for cis determinations the n.m.r. probe was at the same temperature as that of the thermostat being used for the decompositions).

With the *cis*-crotonic acid sequence it had already been discovered (4) that the preparation of acid chloride according to the method of Jones and Mason (1, 3) resulted in a significant proportion of *trans*-crotonyl chloride. That this source of loss of geometry was at least partly responsible for the latter authors' conclusions about the stereochemistry of the azide rearrangement was evident from the next step, conversion to the acyl azide. It had already been ascertained by us that treatment of trans-crotonyl chloride in ether with finely ground sodium azide was sufficient to obtain the azide, conditions which the earlier workers (3) had not only found adequate for the preparation of *trans*-crotonyl azide, but had also found sufficient with ciscrotonyl chloride. We could not react the cis acid chloride with sodium azide in ether even at temperatures 15 °C higher than the earlier work or, to a significant extent, in diethyl triethylene glycol at 65 °C.

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Hence, it is felt that this lack of reactivity of unequivocal cis-crotonyl chloride with sodium azide under these conditions is an additional indication that a significant loss of geometry had already been incurred by Jones and Mason in their preparation of *cis* acid chloride. Therefore, it is postulated that the azide obtained by them was almost certainly largely the *trans* isomer.

Possibly the much greater solubility of a tetralkyl ammonium azide (10) in ether would have given improved results with the cis acid chloride but since aqueous preparation of the

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Decomposition of cis-crotonyl azide at 33 °C

		M	Mole percent of total			
Solvent	Time (h)	<i>cis</i> Azide	<i>trans</i> Azide	<i>cis</i> Iso- cyanate	<i>trans</i> Iso- cyanate	
Deuterio- chloroform	0 4 21 45	84.4 62.8 20.2 4.3	15.6 15.6 15.4 14.6	0 21.6 64.4 77.8	0 0 Trace 3.3	
None	0 6 25 54	84.4 69.2 39.0 15.3	15.6 16.0* 16.5* 18.2*	0 14.8 43.0 63.1	$0 \\ 0 \\ 1.5 \\ 3.4$	
Ether	0 6 25 71	84.4 71.7 50.3 21.9†	15.6 17.2* 18.1* 25.1†	0 11.1 31.5 52.0†	0 0 Trace Trace	
Ether‡	0 18 42	84.4 65.0 32.1†	15.6 18.5* 24.0†	0 16.5 43.3†	0 0 0	

*These give some indication of the extent of loss of the other three components in the run by volatilization or hydrolysis. †The nuclear magnetic resonance samples were very dilute, conse-quently the integrals are not very accurate. ‡Most of the ether was carefully boiled off the aliquots before nuclear magnetic resonance analysis.

cis azide led to good yields of material with good retention of geometry these less accessible azides were not considered further. Both stereochemical and yield objectives were improved by carrying out the aqueous reaction with strong cooling; chloride hydrolysis, isomerization, and decomposition to the isocyanate were all reduced to negligible levels. *cis*-Crotonyl azide of 85–90% correct geometry in 80% or better yields could regularly be obtained by this method.

Important to side-step ambiguity in the final rearrangement step of the sequence was the significantly lower decomposition temperature of *cis*-crotonyl azide over the *trans* isomer. The temperature that was necessary to stop the decomposition of the *cis* isomer was -20 °C whereas, with the trans isomer, 0 °C was sufficient and even at room temperature its rate of decomposition was negligible. In this work decompositions were carried out at 33 °C since at this temperature the cis azide rearranged at an easily measurable rate and the trans azide was still more or less stable. Table IV summarizes these results. The rate of appearance of *cis*-propenyl isocyanate was found to be the same as the rate of loss of cis-crotonyl azide, within experimental error. In spite of precautions against the intrusion of







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FIG. 2. The decomposition of *cis*-crotonyl azide at 33 °C: ○, Ether; △, Ether (rough); □, neat; , CDCl₃.

atmospheric moisture some could have entered when aliquots for analysis were being withdrawn. Hydrolysis of a small portion of the isocyanate to amine with this moisture is probably the explanation for the gradual apparent rise in the proportion of the *trans* azide reported for some of the runs. However, these results show quite conclusively that the rearrangement of *cis*-olefinic acyl azides is stereospecific, at least for *cis*-crotonyl azide.

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The effect of solvent on the decomposition of

cis-crotonyl azide was tested while azide was still available. It was thought quite possible that the stereospecificity of the rearrangement might be affected, but no significant effect on the rate was expected (2). Referring to Table IV, again, one can see no noticeable effect of solvent polarity or lack of solvent altogether on stereospecificity, but even our crude (kinetically speaking) runs show quite a noticeable enhancement of rate in going from a decomposition run in ether, to a run without solvent, to a run in

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deuteriochloroform (see Fig. 2). This is a somewhat surprising result since the Curtius rearrangement is thought to proceed via a unimolecular path (2, 5) but perhaps an azide halflife difference of a factor of 3.7 between the slowest and the fastest reactions is not considered large.

We have no explanation for one apparent anomaly. As traditional confirmation of our n.m.r. findings, conversion with ammonia of portions of the two isomeric isocyanates to the corresponding cis- and trans-propenyl ureas was undertaken. Jones and Mason (1) had found a value of 122 °C for the melting point of transpropenyl urea. Through a number of preparations and recrystallizations we could not duplicate this melting point, even though reasonable analyses were obtained. Perhaps of more importance though, at any stage of the crystallization of either isomeric urea, significant mixture melting point depressions were consistently observed. Also, n.m.r. spectra of the two compounds showed the expected differences (Table II).

Two methods were used to confirm the n.m.r. spectral assignments of the cis- and transpropenyl ureas. The first was by checking the n.m.r. spectra of the urea when one or both of the NH₂ hydrogens were replaced by methyls; this confirmed all the N-H assignments (Table III). The second was addition of D_2O to a hexadeuteriodimethylsulfoxide solution of transpropenyl urea to see if sufficient exchange of the single N—H hydrogen with deuterium could be induced to eliminate the assigned allylic hydrogen coupling with it. About 30% $\mathrm{D}_2\mathrm{O}$ in the solution brought about the collapse of the allylic hydrogen multiplet from at least 14 visible peaks (theoretical = 16) to the 8 seen for allylic hydrogen in spectra of the isocyanates, and a simultaneous loss of the propenyl N-H resonance. This result must be ascribed to elimination of the allylic hydrogen N-H coupling by exchange of the N--H with deuterium, serving as confirmation for the assignment of the single N-H doublet.

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