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2 D D Callander, P L Coe and J C Tatlow, *J Chem Soc Chem. Comm* , 143 (1966)

3 P S Anderson, M.E Christy, G F Lundell and G S Ponticello, *Tetrahedron Letters*, 2553 (1975) This reference described the synthesis of 5,6,7,8-tetrafluoro-1,4-dihydronaphthalen-1,4-imine from which *III*; b p 95-7^o/0 2 mm, δ^{TMS}_{ppm} ($CDCl_3$) 1 3 (CH_3, t, J = 6 3Hz), 4 2 (CH_2, q, J = 6 3Hz), 5.9 (bridgehead H, m) 7 1 (vinyl H, m), m/e 287 (M^+), m/e 261 ($M^+-C_2H_2$), was prepared on treatment with ethyl chloroformate and triethylamine in chloroform

4 B Rice, R J. Galiano and W J Lehmann, *J Phys Chem* , *61*, 1222 (1957)

5 R E Lyle, E.W Southwick and J J Kaminski, *J Am Chem. Soc* , *94*, 1413, (1972)

6 G Gribble, N R Easton, Jr and J.T Eaton, *Tetrahedron Letters*, 1075 (1970)

7 All relative percentages reported in this communication were obtained by glc on a 6' ¼" o d 5% OV 17 on 60-80 mesh chromosorb W column operated at 170^{o}C with a helium flow rate of 32 ml/min

8 *VI* M.P 93-95^o, ν^{Nujol}_{max} 3360 and 1685 cm^{-1}, δ^{TMS}_{ppm} ($CDCl_3$) 1 25 (CH_3, t, J = 6 3Hz), 1 90 (CH_2, m), 2 9 (OH, d, J = 9 5Hz), 4.1 ($O-CH_2$, q, J = 6 3Hz), 4.2 (carbinyl, m, converted to t on exchange with D_2O), 5 3 (bridgehead H, m), 5 45 (bridgehead H, m), m/e 305 (M^+), m/e 261 ($M^+-C_2H_4O$), m/e 189 (isoindole)

9. D J Sandman, K Mislow, W P Giddings, J Dirlan and G C Hanson, *J Am Chem Soc.*, *90*, 4877 (1968)

10 J R Parikh and W von E Doering, *J Am Chem Soc* , *89*, 5505 (1967) Use of the sulfur trioxide complex of trimethylamine rather than that of pyridine as described in this reference avoids the annoying problem of separating pyridine from basic products.

11 A P Marchand and R W Allen, *Tetrahedron Letters*, *67* (1975).

12 Compare the spectrum of *IV* with that shown by Marchand (ref 11) for N-methyl-7-aza-2,3-benzo-*exo*-5-deuterionorbornene The lithium aluminum deutride reduction of *VII* to yield *exo*-2-deuterio *II*, δ^{TMS}_{ppm} ($CDCl_3$) 1 0 (H_{3n}, d, $J_{3n,3x}$ = 12 3Hz) 2 55 (H_{3x}, dd, $J_{3x,3n}$ = 12 3Hz, $J_{3x,4}$ = 4 8Hz), also supported these assignments. The *exo* proton H_{3x} is coupled to the bridgehead proton H_4, while the *endo* proton H_{3n} is not.

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16 Correct analytical data were obtained for all new compounds

Tetrahedron Letters No. 15, pp 1145 - 1148, 1976. Pergamon Press. Printed in Great Britain.

THE PREPARATION OF UREAS BY THE THERMOLYSIS OF ALLYLIC PSEUDOUREAS

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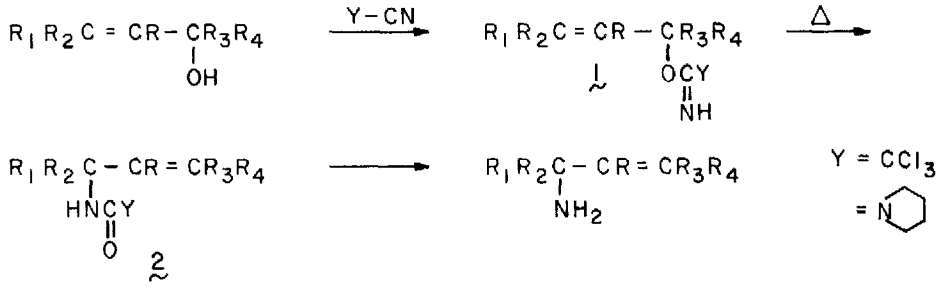
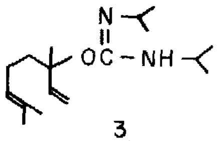
Previous reports from our laboratory have demonstrated that the thermal and catalyzed [3.3]-sigmatropic rearrangement of allylic trichloroacetimidates constitutes a useful synthetic method for the 1,3-transposition of oxygen and nitrogen functional groups (Scheme I, Y = CCl_3).[2,3] In the interest of generalizing this method to other imine derivatives, and in the hope that an electron donating imine substituent would suppress the competing elimination reaction observed with trichloroacetimidic esters of 3-substituted-2-cyclohexene-1-ols,[3] we have studied the thermolysis of allylic pseudoureas (Scheme I, Y = N⬡) This letter constitutes the first report of the thermal [3.3]-sigmatropic rearrangement of allylic pseudoureas.[4,5]



SCHEME I

Several methods are available for the preparation of pseudoureas from alcohols.[6] We have found that primary and secondary alcohols readily undergo alkoxide catalyzed addition to N-cyanopyrrolidine,[7] at or below room temperature, to yield the corresponding pseudoureas 1, (Y = N⬠) in crude yields of 85% or better.[8] This mild method failed with linalool, however condensation with diisopropylcarbodiimide under similar conditions afforded pseudourea 3 in 70% yield. The pseudourea intermediates were not purified, but were directly rearranged to 2 (Y = N⬠) in refluxing xylene (137°) or decalin (130°). The overall yields of the rearranged ureas (Table I) are in most cases good and are similar to the yields of 2 (Y = CCl_3) obtained *via* the corresponding trichloroacetimidate intermediates.[2,3] The yield of 8 constitutes some improvement over the previous method[3]. Ureas 5 and 6 were formed highly stereoselectively since less than 2% of the corresponding (Z)-stereoisomers were formed. Thermolysis of the pseudourea derivatives of alcohols 4 and 7 (R = $(CH_2)_3CH$⬠) was not regiospecific since 9 (9%) and 10 (14%) were also isolated[9] This later result presumably indicates a contribution in these cases from a two-step reaction pathway



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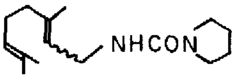

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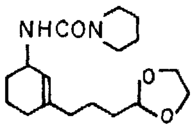

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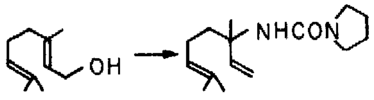
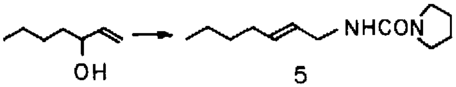
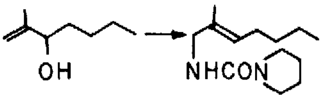
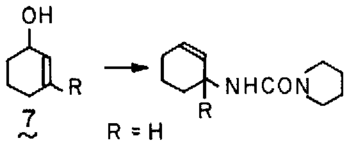
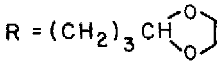
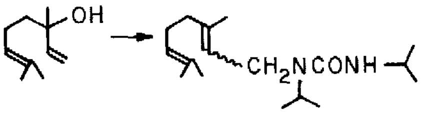
Since the product ureas are more difficult to convert to the parent amines than the corresponding trichloroacetamides, the imidate procedure[2,3] is clearly preferred for the allylic transposition of OH and NH_2 groups. The pseudourea rearrangement reported here, however, should be a valuable method for the preparation of unsymmetrical N,N,N'-trisubstituted-ureas.

The following procedures are representative·

2-Methyl-1-heptene-3-yl 1-pyrrolidinecarboximidate (11). A solution of 2-methyl-1-hepten-3-ol (2.56 g, 20 mmol) in 5 ml of THF was treated with KH (0.48g, mineral oil suspension, 3.0 mmol) and the resulting solution was added dropwise to a solution of 1-cyanopyrrolidine[7] (1.92g, 20 mmol) in 10 ml of THF at -5 to -10°. After stirring at 25° for 20 hr the solution was concentrated, hexane (containing 3 mmol of acetic acid) was added, the mixture was shaken for 1 min, and a small amount of insoluble residue was removed by filtration. Concentration afforded 3.87g (88%) of essentially pure 11.

N-[(E)-2-methyl-2-hepten-1-yl]-1-pyrrolidinecarboxamide (6). A solution of 1.90g of 11 and 40 ml of xylene was heated at reflux for 9 hr Upon cooling to 25°, 43 mg

TABLE I 1,3-Conversion of an Allylic Alcohol to an Allylic Urea [11]

CONVERSION	CONDITIONS	YIELD (%)	mp (°C)
 4	137°, 80 hr	54	37-38
 5	137°, 13 hr	81	77-78
 6	137°, 9 hr	63	89.5-90 5
 7 R = H	137°, 20 hr	60	92 5-93
 8	130°, 24 hr	28	62-64
	130°, 30 min	61	oil

(4.5%) of 1-pyrrolidinecarboxamide (mp 210-213°)[10] was isolated by filtration. Concentration of the filtrate gave a semi-solid which was treated with hexane to yield 1.26g of **6**, mp 89-90°. An additional 0.11g of **6** (total yield 1.37g, 63% for the two steps) was obtained by chromatography of the residue on alumina (1:1 hexane:dichloromethane). One recrystallization from hexane afforded the analytical sample: mp 89.5 - 90.5°, ν_{max}(KBr) 3280, 1650, 1540 cm^{-1}, pmr ($CDCl_3$, δ) 5.25 (t, J=7, -C$\underline{H}$=), 4.23 (broad s, NH), 3.73 (d, J=6, C$\underline{H}_2$-NH), 3.1 - 3.5 (m, pyrrolidine C-2 and C-5 methylenes), 1.7 - 2.2 (m, pyrrolidine C-3 and C-4 methylenes), and 1.60 ppm (s, =C-C$\underline{H}_3$). *Anal* ($C_{13}H_{24}N_2O$) C, H, N.

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References and Notes

1. Alfred P. Sloan Foundation Fellow, 1975-1977
2. L.E. Overman, *J. Amer. Chem. Soc.*, *96*, 597 (1974); L.E. Overman, *ibid.*, *98*, in press.
3. L.E. Overman, *Tetrahedron Letters*, 1149 (1975).
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5. A somewhat related rearrangement of 3-allyloxy-1,2,4-benzothiadiazine-1,1-dioxides was recently reported: P. Pecorari, A. Albasini, and L. Raffa, *Farmaco, Ed. Sci.*, *28*, 203 (1973).
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9. All isomers were stable under the thermolysis conditions.
10. German Patent 852,999 (1952); *Chem. Abstr.*, *52*, P11127a (1958).
11. Satisfactory ir, nmr, and combustion analysis data were obtained for all new compounds.