NICKEL-CATALYZED REACTIONS OF THIAZOLES, ISOXAZOLES, OXAZOLINES AND THIAZOLINES WITH GRIGNARD REAGENTS[1]

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Dedicated to the memory of the late Professor Tetsuji Kametani.

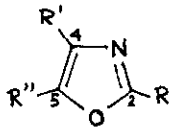
Abstract- Grignard reagents convert thiazoles, isoxazoles, oxazolines and thiazolines into N-vinylimines, β-amino-α,β-unsaturated ketones, tetrahydrooxazoles and tetrahydrothiazoles, respectively, under the influence of phosphine-ligated nickel species. The reaction characteristics and the uncatalyzed reactions are described.

A few years ago, it was shown that aromatic, five-membered heterocycles, such as furan, thiophene, selenophene and tellurophene, undergo reaction with Grignard reagents in the presence of 1,3-bis(diphenylphosphino)propanenickel dichloride ((dppp)$NiCl_2$), producing 1,4-dialkylated 1,3-butadienes (equation **I**).[2] It now became of interest to learn whether the new reaction would tolerate a second hetero atom (i.e. a nitrogen) in the heterocycle and the following study was undertaken.

Y = O, S, Se or Te

$$\xrightarrow[(dppp)NiCl_2]{RMgBr} RCH{=}CHCH{=}CHR \qquad (I)$$

The first test appeared to be a bad omen, as the oxazoles **1** proved to be inert toward phenylmagnesium bromide either in an unaided manner or in the presence of (dppp)$NiCl_2$.

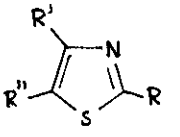


1

a, R = R″ = C_6H_5, R′ = H

b, R = R′ = C_6H_5, R″ = H

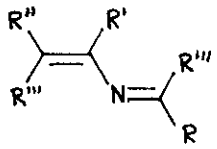
c, R = Me, R′= C_6H_5, R″ = H



2

Thiazoles (**2**), however, underwent the reaction with a Grignard reagent in the anticipated fashion. Thus exposure of thiazoles **2a**[3], **2b**[4] and **2c**[5] to phenylmagnesium bromide under the influence of (dppp)$NiCl_2$ let to N-vinylimines **3a** (60% yield), **3b** (67%) and **3c** (71%), respectively.[6] Whereas the thiazoles were generally inert in reactions without

nickel species, heterocycle **2c** underwent dimerization in the presence of phenylmagnesium bromide (the latter acting presumably as a base), forming thiazolothiazoline **4**[7] (72%). (Dppp)$NiCl_2$-induced interaction of the thiazoles **2** with methylmagnesium bromide produced metastable N-vinylimines **3d** (20%), **3e** (60%), and **3f** (54%), respectively, whose mild hydrolysis in ethanolic 1% hydrochloric acid solution yielded (ca. 90%) α-phenylpropionaldehyde and acetophenone, propiophenone and acetophenone, and propiophenone, respectively.



3

a, R = R″ = R‴ = C_6H_5, R′ = H

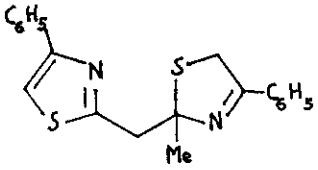
b, R = R′ = R‴ = C_6H_5, R″ = H

c, R = Me, R′ = R‴ = C_6H_5, R″ = H

d, R = R″ = C_6H_5, R′ = H, R‴ = Me

e, R = R′ = C_6H_5, R″ = H, R‴ = Me

f, R = R‴ = Me, R′ = C_6H_5, R″ = H



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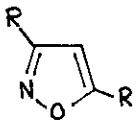
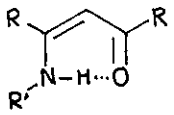


5a, R = Me

b, R = t-Bu



6a, R = Me, R′ = H

b, R = Me, R′ = C_6H_5

c, R = Me, R′ = C_6H_4 Me(*p*)

d, R = t-Bu, R′ = H

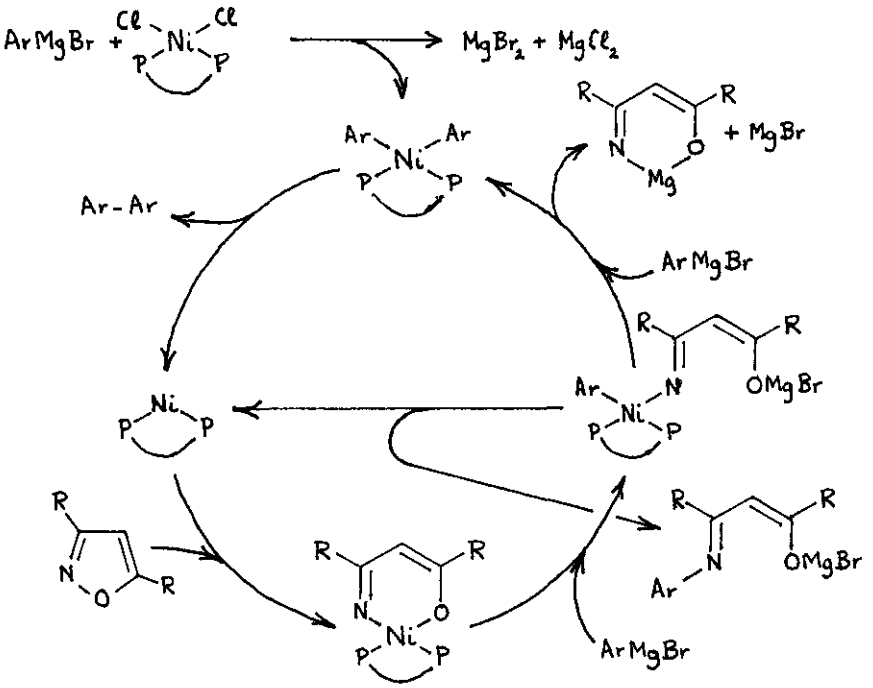
Isoxazoles revealed completely different Grignard reaction chemistry. Interaction of 2,4-dimethylisoxazole (**5a**) with methylmagnesium bromide (2 equiv.) led quantitatively to the reduction product **6a**, the latter being also the product (95%) of the same reaction in the presence of (dppp)$NiCl_2$. Exposure of isoxazole **5a** to phenylmagnesium bromide (2 equiv.) yielded reduction product **6a**[8] (55%), oxidation product biphenyl (90%) and N-phenylation product 6b[8] (5%). The use of (dppp)$NiCl_2$ for the reaction changed the product ratio: **6a** (61%), biphenyl (82%) and **6b** (24%). Finally, the presence of [1,1'-bis(diphenylphosphino)ferrocene]nickel dichloride ((dppf)$NiCl_2$)[9] altered the product distribution strongly in favor of the N-phenyl derivative: **6a** (5%), biphenyl (10%) and **6b** (85%). A (dppf)$NiCl_2$-induced reaction between isoxazole **5a** and *p*-tolylmagnesium bromide led to a similar observation: **6a** (7%), di-*p*-tolyl (12%) and **6c**[10] (60%).

In order to ascertain the effect of steric factors on the Grignard reactions of isoxazoles, heterocycle **5b**[11] was submitted to reactions with phenylmagnesium bromide. In the absence of any nickel species no reaction took place (82% recovery of **5b**), whereas under the influence of (dppp)$NiCl_2$ or (dppf)$NiCl_2$ the reaction proceeded to yield reduction product **6d** (86 and 66%, respectively) and oxidation product biphenyl (95 and 83%).

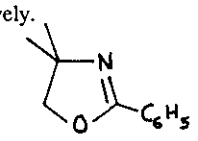
As noted earlier,[12] Grignard reagents reduce isoxazoles by nitrogen-oxygen bond cleavage. The new facts emerging from the above results are (a) the suppression of the reduction by bulky groups next to the reaction site and (b) a low-level competition with the reduction by an N-arylative ring opening on use of an arylmagnesium reagent. Finally,

nickel catalysis overcomes steric retardation of the heterocycle reduction and enhances the N-arylation pathway.[13] Scheme I illustrates the likely catalytic cycle for the nickel-induced reactions of 2,4-dialkylisoxazoles with arylmagnesium bromide.[14]

Scheme I



Oxazoline 7 and Thiazoline 9a. Alongside the above studies on oxazoles and thiazoles the aforementioned dihydro derivatives were investigated. Whereas oxazoline **7**[15] was inert to Grignard reagents, the presence of (dppp)$NiCl_2$ induced an addition process to take place. Thus nickel-catalyzed reaction of oxazoline **7** with methyl-, *n*-butyl- and phenyl-magnesium bromide afforded tetrahydrooxazoles **8a** (70%), **8b** (62%) and **8c** (90%), respectively. Thiazoline **9a**, prepared by treatment of 2-benzamido-2-methylpropanol[16] with phosphorus pentasulfide[17], proved to be inert to methylmagnesium bromide, but was transformed into thiazolines **9b** (64%) and **9c** (58%) on exposure to phenyl- and *p*-tolyl-magnesium bromides, respectively.[18] On the other hand, interaction of thiazoline **9a** with methyl- and phenylmagnesium bromides with the aid of (dppp)$NiCl_2$ furnished tetrahydrothiazoles **10a** (58%) and **10b** (70%), respectively.



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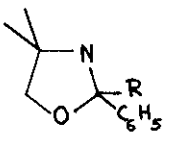
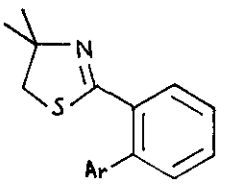
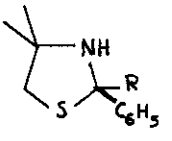


8a, R = Me
b, R = *n*-Bu
c, R = C_6H_5



9a, Ar = H
b, Ar = C_6H_5
c, Ar = $C_6H_4Me(p)$



10a, R = Me
b, R = C_6H_5

EXPERIMENTAL

Melting points were taken on a Reichert micro hotstage and are uncorrected. Infrared spectra of chloroform solutions were observed on Pye-Unicam 3-200 and Perkin-Elmer 1330 spectrophotometers. ^{1}H Nmr spectra of $CDCl_3$ solutions with internal Me_4Si standard were recorded on Varian EM-390 and 360 MHz (a highly modified Varian HR-220 console with an Oxford magnet and a Nicolet 1180-E computer system) spectrometers. ^{13}C Nmr spectra of $CDCl_3$ solutions were determined on a Nicolet NT-200 (wide-bore, broad-band and Oxford magnet containing) spectrometer operating in the Fourier transform mode. The carbon shifts are in ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. All Grignard reactions were performed under argon and in freshly distilled, dry solvents. Crude product solutions were dried over Na_2SO_4.

N-Vinylimines 3. An ethereal 2.9 M methylmagnesium bromide (0.20 mmol) solution was added dropwise to a stirring suspension of 54 mg (0.10 mmol) of (dppp)$NiCl_2$ in 10 ml of benzene for catalyst reduction and the stirring continued at room temperature for 0.5 h. An ethereal 3.0M phenylmagnesium bromide (2.20 mmol) solution and subsequently 237 mg (1.00 mmol) of 2,5-diphenylthiazole (**2a**)[3] were added and the stirring mixture refluxed for 15 h. Saturated $NaHCO_3$ solution was added to the cooled mixture and the combination extracted with ether. The extract was dried and evaporated. Chromatography on Florisil yielded 215 mg (60%) of crystalline imine **3a**: mp 176-178°C; ir C=N, C=C 1660 (s) cm^{-1}; ms 359 (M^+, 90), 282 (base), 208 (33), 165 (60), 129 (42), 28 (74). Exact mass: *m/z* 359.1670 (Calcd for $C_{27}H_{21}N$: 359.1674).

The identical reaction and work-up of 237 mg (1.00 mmol) of 2,4-diphenylthiazole (**2b**)[4] furnished 242 mg (67%) of crystalline imine **3b**: mp 132-134°C; ir C=N, C=C 1590 (s) cm^{-1}; ^{1}H nmr δ 6.06 (s, 1, vinyl H), 6.5-8.1 (m, 20, aryl Hs); ms 359 (M^+,21), 197 (base), 183 (83), 105 (67), 91 (29). Exact mass: *m/z* 359.1690 (Calcd for $C_{27}H_{21}N$: 359.1674).

The identical reaction and work-up for 175 mg (1.00 mmol) of 2-methyl-4-phenylthiazole (**2c**)[5] led to 210 mg (71%) of crystalline imine **3c**: mp 101-102° C; ir C=N, C=C 1600 (s) cm^{-1}; ^{1}H nmr δ 2.06 (s, 3, Me), 6.37 (s, 1, vinyl H), 7.0-7.7 (m, 13, aryl Hs), 7.9-8.2 (m, 2, aryl Hs); ms 297 (M^+, base), 282 (31), 179 (53), 178 (49), 103 (30). Exact mass: *m/z* 297.1540 (Calcd for $C_{22}H_{19}N$: 297.1516).

The preparation of the vinylimines **3d-f** differed from the above by the replacement of reacting Grignard reagent by an ethereal 2.9 M methylmagnesium bromide (2.20 mmol) solution, by refluxing being extended to 24 h and by the product purification taking place by flash chromatography (hexane elution) on Florisil. Thus 237 mg (1.00 mmol) of 2,5-diphenylthiazole (**2a**)[3] was converted into 47 mg (20%) of colorless, liquid, highly unstable imine **3d**: ir C=N, C=C 1580 (s) cm^{-1}; ^{1}H nmr δ 1.90 (s, 3, Me), 2.50 (s, 3, α-imino Me), 6.55 (s, 1, vinyl H), 7.1-7.7 (m, 8, aryl Hs), 7.9-8.2 (m, 2, aryl Hs).

The identical reaction and work-up on 237 mg (1.00 mmol) of 2,4-diphenylthiazole (**2b**)[4] gave 141 mg (60%) of colorless, liquid, highly labile imine **3e**: ir C=N, C=C 1580 (s) cm^{-1}; ^1H nmr δ 1.53 (d, 3, J = 7 Hz, Me), 2.12 (s, 3, α-imino Me), 5.40 (q, 1, J = 7 Hz, vinyl H), 7.1-7.6 (m, 6, aryl Hs), 7.8-8.1 (m, 4, aryl Hs).

The identical reaction and work-up of 175 mg (1.00 mmol) of 2-methyl-4-phenylthiazole (**2c**)[5] afforded 94 mg (54%) of colorless, liquid, metastable imine **3f**: ir C=N, C=C 1582 (s) cm^{-1}; ^1H nmr δ 1.52 (d, 3, J = 7 Hz, Me), 1.73, 2.16 (s, 3 each, α-imino methyls), 5.37 (q, 1, J = 7 Hz, vinyl H), 7.1-7.6 (m, 5, aryl Hs).

Thiazole Dimer 4.[7] A solution of 175 mg (1.00 mmol) of 2-methyl-4-phenylthiazole (**2c**)[5] and 1.20 mmol of phenylmagnesium bromide in 10ml of benzene was refluxed for 10 h. It was cooled, saturated $NaHCO_3$ solution added and the mixture extracted with ether. The extract was dried and evaporated. Flash chromatography (20:1 C_6H_{14}-EtOAc elution) on Florisil yielded 252 mg (72%) of colorless, liquid dimer **4**[7]: ^1H Nmr spectrally identical with recorded data.[7]

Vinylogous Amides 6. An ethereal 3.0 M methylmagnesium bromide (12.0 mmol) solution was added to a solution of 485 mg (5.00 mmol) of 3,5-dimethylisoxazole (**5a**) in 20 ml of benzene and the mixture refluxed for 5 h. Saturated NH_4Cl solution was added to the cooled solution and the mixture extracted with ether. The extract was dried and evaporated. Chromatography (20:1 C_6H_{14}-EtOAc elution) on silica gel afforded 988 mg (quantitative yield) of crystalline 4-amino-3-penten-2-one (**6a**)[8]: mp 41-42° C (C_6H_{14}) (lit.[8] mp 43° C); ir NH 3350 (m), 3160 (m), C=O, C=C 1620 (s) cm^{-1}; ^1H nmr δ 1.90, 2.00 (s, 3 each, methyls), 4.96 (s, 1, H-3), 5.75, 9.70 (br s, 1 each, NH_2).

The identical reaction and work-up except for the replacement of MeMgBr by an ethereal 3.0 M phenylmagnesium bromide (12.0 mmol) solution led to 1.38 g (90%) of biphenyl: mp 68-69° C, 272 mg (55%) of 4-amino-3-penten-2-one (**6a**)[8]: mp 41-42° C, and 87 mg (5%) of crystalline 4-anilino-3-penten-2-one (**6b**)[8]: mp 45-47° C (C_6H_{14}) (lit.[8] mp 47° C); ^1H nmr δ 1.96, 2.18 (s, 3 each, methyls), 5.12 (s, 1, H-3), 6.9-7.5 (m, 5, aryl Hs), 12.45 (br s, 1, NH); ms 175 (M^+, 61), 161 (89), 158 (39), 132 (59), 118 (base), 93 (36), 84 (33), 77 (56), 65 (48).

An ethereal 2.9 M methylmagnesium bromide (2.00 mmol) solution was added to a stirring suspension of 540 mg (1.00 mmol) of (dppp)$NiCl_2$ in 20 ml of benzene for catalyst reduction and the stirring continued at room temperature for 0.5 h. An ethereal 3.0 M methylmagnesium bromide (24.0 mmol) solution and subsequently 970 mg (10.0 mmol) of 3,5-dimethylisoxazole (**5a**) were added and the stirring mixture refluxed for 5 h. Work-up as above produced 940 mg (95%) of 4-amino-3-penten-2-one (**6a**).

The identical reaction and work-up except for the replacement of MeMgBr by an ethereal 3.0 M phenylmagnesium bromide (24.0 mmol) solution yielded 1.26 g (82%) of biphenyl, 603 mg (61%) of 4-amino-3-penten-2-one (**6a**)[8] and 402 mg (24%) of 4-anilino-3-penten-2-one (**6b**).[8]

A reaction and work-up identical with the last one except for the replacement of the catalyst by 68 mg (0.10 mmol) of (dppf)$NiCl_2$[9] produced 155 mg (10%) of biphenyl, 50 mg (5%) of 4-amino-3-penten-2-one (**6a**)[8] and 1.48 g (85%) of 4-anilino-3-penten-2-one (**6b**).[8]

Modification of the last reaction and work-up by replacement of C_6H_5MgBr by an ethereal 2.2 M *p*-tolylmagnesium bromide (24.0 mmol) solution led to 218 mg (12%) of di-*p*-tolyl, 69 mg (7%) of 4-amino-3-penten-2-one (**6a**)[8] and 1.13 g (60%) of crystalline 4-(*p*-toluidino)-3-penten-2-one (**6c**)[10]: mp 65-66° C (C_6H_{14}) (lit.[10] 68° C); ^1H nmr δ 1.90, 2.06 (s, 3 each, methyls), 2.30 (s, 3, aryl Me), 5.10 (s, 1, H-3), 6.8-7.2 (m, 4, aryl Hs), 7.40 (br s, 1, NH).

Modification of the above C_6H_5MgBr/(dppp)$NiCl_2$/**5a** reaction and work-up by replacement of the heterocycle by 181 mg (1.00 mmol) of 3,5-di-*t*-butylisoxazole (**5b**)[11] and reduction of the amount of the catalyst to 54 mg (0.10 mmol) of (dppp)$NiCl_2$ and of reagent to a 3.0 M phenylmagnesium bromide (2.2 mmol) solution furnished 146 mg (95%) of biphenyl and 157 mg (86%) of crystalline 2,2,6,6-tetramethyl-5-amino-4-hepten-3-one (**6d**): mp 131-132° C (C_6H_{14}); ^1H nmr δ 1.13, 1.22 (s, 9 each, methyls), 5.34 (s, 1, H-4); ms 183 (M^+, 6), 126 (base). Exact mass: *m/z* 183.2933 (Calcd for $C_{11}H_{21}ON$: 183.2930).

A reaction and work-up identical with the last one except for the replacement of the catalyst by 7.0 mg (0.01 mmol) of (dppf)$NiCl_2$ afforded 128 mg (83%) of biphenyl and 120 mg (66%) of crystalline 2,2,6,6-tetramethyl-5-amino-4-hepten-3-one (**6d**).

Tetrahydrooxazoles 8. An ethereal 2.9 M methylmagnesium bromide (0.40 mmol) solution was added dropwise to a stirring suspension of 108 mg (0.20 mmol) of (dppp)$NiCl_2$ in 15 ml of benzene for catalyst reduction and the stirring mixture refluxed for 15 min. An ethereal 2.9 M methylmagnesium bromide (2.20 mmol) solution and subsequently 350 mg (2.00 mmol) of 2-phenyl-4,4-dimethyl-Δ^2-oxazoline (**7**)[15] were added and the black, stirring mixture refluxed for 15 h. Saturated $NaHCO_3$ solution was added to the cooled mixture and the combination extracted with ether. The extract was dried and evaporated. Chromatography (C_6H_{14} elution) of the residue on Florisil gave 267 mg (70%) of colorless, liquid 2-phenyl-2,4,4-trimethyloxazolidine (**8a**): ir NH 3060 (w), 2965 (m), C=C 1600 (m) cm^{-1}; ^1H nmr δ 0.93, 1.30, 1.60 (s, 3 each, methyls), 3.46, 3.53 (d, 1 each, J = 8 Hz, C-5 Hs), 7.1-7.5 (m, 5, aryl Hs); ^{13}C nmr δ 27.1 (4-Me), 28.5 (4-Me), 30.9 (2-Me), 59.7 (C-4), 77.2 (C-5), 97.4 (C-2), 125.2 (*p*-C), 126.8 (*m*-C), 127.7 (*o*-C) 146.2 (*ipso*-C); ms 191 (M^+,6), 176 (base), 160 (24), 114 (33), 105 (38), 77 (36), 72 (27), 55 (21), 42 (29). Exact mass: *m/z* 191.1304 (Calcd for $C_{12}H_{17}ON$: 191.1310).

The identical reaction except for the replacement of MeMgBr by an ethereal 2.3 M *n*-butylmagnesium bromide (3.50 mmol) solution and the use of 493 mg (2.88 mmol) of starting heterocycle as well as work-up except for 50:1 C_6H_{14}-EtOAc elution yielded 405 mg (62%) of colorless, liquid 2-*n*-butyl-4,4-dimethyl-2-phenyloxazolidine (**8b**): ir NH 3059 (w), 2965 (m), C=C 1600 (m) cm^{-1}; ^1H nmr δ 0.76 (t, 3, J = 7 Hz, butyl Me), 0.90, 1.26 (s, 3 each, methyls), 1.0-2.5

(m, 6, methylenes), 3.43, 3.53 (d, 1 each, J = 8 Hz, C-5 Hs), 7.1-7.6 (m, 5, aryl Hs); ^{13}C nmr δ 13.7 (butyl Me), 22.9 (butyl C-3), 27.5 (4-Me), 29.2 (4-Me), 31.5 (butyl C-2), 34.6 (butyl C-1), 59.9 (C-4), 77.2 (C-5), 98.1 (C-2), 125.3 (*p*-C), 126.9 (*m*-C), 127.8 (*o*-C), 145.8 (*ipso*-C); ms 233 (M^+, 5), 176 (base), 105 (50), 77 (48), 55 (20), 41 (23), 29 (34). Exact mass: *m/z* 233.1784 (Calcd for $C_{15}H_{23}ON$: 233.1779).

A reaction and work-up (20:1 C_6H_{14}-EtOAc elution) identical with the above **7**→ **8a** transformation except for the replacement of MeMgBr by an ethereal 2.0 M phenylmagnesium bromide (2.20 mmol) solution furnished 455 mg (90%) of crystalline 4,4-dimethyl-2,2-diphenyloxazolidine (**8c**): mp 65-66° C (C_6H_{14}); ir NH 3320 (w), 2960 (m), C=C 1600 (m) cm^{-1}; ^{1}H nmr δ 1.15 (s, 6, methyls), 3.63 (s, 2, C-5 Hs), 7.1-7.7 (m, 10, aryl Hs); ^{13}C nmr δ 27.7 (methyls), 60.1 (C-4), 77.3 (C-5), 99.8 (C-2), 125.7 (*p*-C), 127.0 (*m*-C), 127.9 (*o*-C), 145.5 (*ipso*-C); ms 252 (M^+-1, 5), 222 (20), 176 (base), 165 (22), 105 (62), 77 (47). Exact mass (M^+ -1): *m/z* 252.1380 (Calcd for $C_{17}H_{18}ON$: 252.1388).

Thiazolines 9. A mixture of 5.00g (0.025 mmol) of 2-benzamido-2-methylpropanol[16] and 2.70 g (0.052 mmol) of phosphorus pentasulfide was heated at 110° C in an open container.[17] After the reaction had started, the temperature was maintained for 20 min. Water (50 ml) was added to the cooled mixture and the latter extracted with methylene chloride. The extract was dried and evaporated. Chromatography of the residue on silica gel and elution with 20:1 C_6H_{14}-EtOAc yielded 3.20 g (64%) of colorless, liquid 4,4-dimethyl-2-phenyl-Δ^2-thiazoline (**9a**): ir C=N 1605 (w), C=C 1575 (m) cm^{-1}; ^{1}H nmr δ 1.44 (s, 6, methyls), 3.16 (s, 2, C-5 Hs), 7.2-7.4 (m, 3, aryl Hs), 7.7-7.9 (m, 2, aryl Hs); ^{13}C nmr δ 27.4 (methyls), 44.9 (C-5), 78.7 (C-4), 128.1 (*p*-C), 128.2 (*m*-C), 130.8 (*o*-C), 133.3 (*ipso*-C), 163.9 (C-2); ms 191 (M^+, 32), 176 (39), 145 (34), 104 (59), 88 (base), 77 (22), 73 (28), 55 (51). Exact mass: *m/z* 191.2913 (Calcd for $C_{11}H_{13}NS$: 191.2904).

An ethereal 3.0 M phenylmagnesium bromide (3.00 mmol) solution was added to a solution of 463 mg (2.42 mmol) of thiazoline **9a** in 20 ml of benzene and the mixture refluxed for 5 h. Saturated NH_4Cl solution was added and the mixture extracted with ether. The extract was dried and evaporated. Chromatography of the residue on silica gel and elution with 50:1 C_6H_{14} -EtOAc led to 375 mg (64%) of colorless, liquid 4,4-dimethyl-2-(*o*-biphenylyl)-Δ^2-thiazoline (**9b**): ir (Nujol) C=N 1620 (w), C=C 1580 (m) cm^{-1}; ^{1}H nmr δ 1.30 (s, 6, methyls), 3.07 (s, 2, C-5 Hs), 7.1-7.6 (m, 9, aryl Hs); ^{13}C nmr δ 26.8 (methyls), 46.2 (C-5), 78.4 (C-4), aryl methines: 126.9, 127.0, 127.7, 128.8, 129.1, 129.5, 130.0, 133.3 (thiazoline-bearing *ipso*-C), aryl *ipso* carbons: 140.2, 140.8, 165.0 (C-2); ms 267 (M^+, 34), 266 (78), 179 (base), 165 (26), 88 (58), 55 (35). Exact mass: *m/z* 267.1023 (Calcd for $C_{17}H_{17}NS$: 267.1020).

The identical reaction and work-up except for the replacement of phenylmagnesium bromide by an ethereal 2.2 M *p*-tolylmagnesium bromide (3.00 mmol) solution furnished 394 mg (58%) of colorless, liquid *o*-[2-(4,4-dimethyl-Δ^2-thiazolinyl)]-(*p*-tolyl)benzene (**9c**): ir C=N 1620 (w), C=C 1580 (m) cm^{-1}; ^{1}H nmr δ 1.32 (s, 6, methyls), 2.37 (s, 3, aryl Me), 3.05 (s, 2, C-5 Hs), 7.1-7.8 (m, 8, aryl Hs); ^{13}C nmr δ 21.0 (aryl Me), 26.8 (methyls), 46.2 (C-5), 78.3 (C-4), 127.8 (*p*-tolyl *m*-C), 129.1 (*p*-tolyl *o*-C), aryl methines: 127.2, 128.7, 129.4, 130.0, 133.5 (thiazoline-bearing *ipso*-C),

aryl *ipso* carbons: 140.3, 140.7, 165.0 (C-2); ms 281 (M^+, 14), 280 (33), 193 (base). Exact mass: *m/z* 281.1220 (Calcd for $C_{18}H_{19}NS$: 281.1214).

Tetrahydrothiazoles 10. An ethereal 2.9 M methylmagnesium bromide (0.32 mmol) solution was added dropwise to a stirring suspension of 87 mg (0.16 mmol) of (dppp)$NiCl_2$ in 15 ml of benzene for catalyst reduction and the stirring mixture refluxed for 15 min. An ethereal 2.9 M methylmagnesium bromide (2.00 mmol) solution and subsequently 317 mg (1.66 mmol) of thiazoline **9a** in 10 ml of benzene were added and the black, stirring mixture refluxed for 13 h. Saturated $NaHCO_3$ solution was added to the cooled mixture and the combination extracted with ether. The extract was dried and evaporated. Chromatography (50:1 C_6H_{14}-EtOAc elution) of the residue on Florisil gave 199 mg (58%) of colorless, liquid 2,4,4-trimethyl-2-phenylthiazolidine (**10a**): ir NH 3010 (w), 2970 (m), C=C 1605 (m) cm^{-1}; ^1H nmr δ 0.96, 1.39, 1.79 (s, 3 each, methyls), 2.85 (s, 2, C-5 Hs), 7.1-7.3 (m, 3, aryl Hs), 7.6-7.7 (m, 2, aryl Hs); ^{13}C nmr δ 27.5 (4-Me), 28.9 (4-Me), 36.1 (2-Me), 48.8 (C-5), 66.7 (C-4), 81.4 (C-2), 125.8 (*m*-C), 126.3 (*p*-C), 127.3 (*o*-C), 148.9 (*ipso*-C); ms 207 (M^+, 26), 192 (47), 160 (77), 120 (base), 104 (32), 77 (24), 69 (24), 55 (28), 42 (40). Exact mass: *m/z* 207.1079 (Calcd for $C_{12}H_{17}NS$: 207.1081).

An identical reaction and work-up except for the replacement of methylmagnesium bromide by an ethereal 3.0 M phenylmagnesium bromide (2.00 mmol) solution and the use of 310 mg (1.62 mmol) of thiazoline **10a** led to 305 mg (70%) of colorless, liquid, 4,4-dimethyl-2,2-diphenylthiazolidine (**10b**): ir NH 2970 (m), C=C 1598 (m) cm^{-1}; ^1H nmr δ 1.23 (s, 6, methyls), 2.85 (s, 2, C-5 Hs), 7.1-7.7 (m, 10, aryl Hs); ^{13}C nmr δ 28.5 (methyls), 49.2 (C-5), 67.3 (C-4), 87.9 (C-2), 126.8 (*p*-C), 126.9 (*m*-C), 127.7 (*o*-C), 147.5 (*ipso*-C); ms 269 (M^+, 53), 236 (26), 222 (base), 182 (38), 165 (21), 104 (51), 84 (37), 77 (33), 49 (46). Exact mass: *m/z* 269.1230 (Calcd for $C_{17}H_{19}NS$: 269.1238).

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