Grubbs and Wilkinson catalyzed reactions of 2-phenyl-3-vinyl substituted 2*H*-azirines

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Dedicated to Professor Lubor Fišera on the occasion of his 60th anniversary

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Abstract

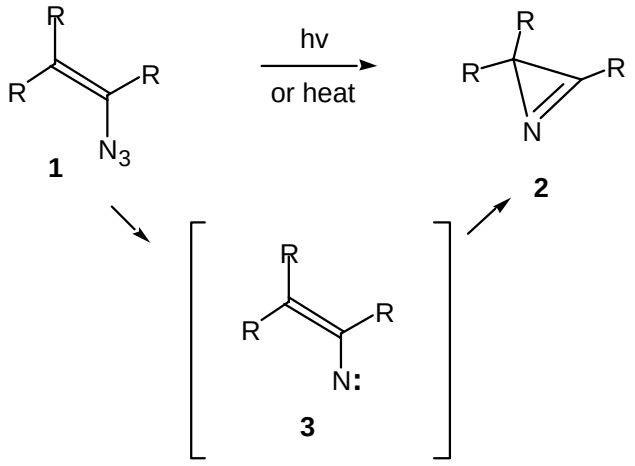
Treatment of 2-phenyl-3-vinyl-substituted 2*H*-azirines with Grubbs' catalyst induces a clean rearrangement and affords products derived from carbon-nitrogen bond cleavage of the 2*H*-azirine ring. However, when the reaction was carried out using Wilkinson's catalyst in an alcoholic solvent, the only product obtained in high yield corresponded to an α,β-unsaturated oxime

Keywords: 3-Vinyl 2*H*-azirine, transition metal, catalyzed, rearrangement

Introduction

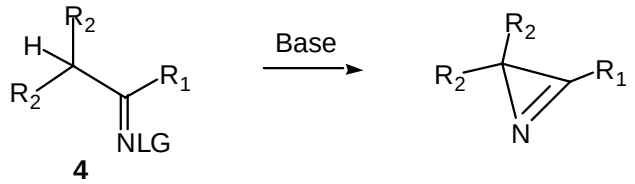
2*H*-Azirines (**2**) are highly reactive three-membered unsaturated nitrogen-containing heterocycles that have been used for the preparation of a wide range of polyfunctional acyclic and cyclic nitrogen containing compounds.[1] This small membered ring can take part in various chemical transformations since it can act as a dienophile or as a dipolarophile and can also function as an electrophile or nucleophile. The ring strain undoubtedly contributes to the high reactivity of the 2*H*-azirine moiety and makes it an attractive intermediate for the preparation of complex heterocyclic ring systems.

A number of synthetic methods are available for forming 2*H*-azirines and include intramolecular reactions of *N*-functionalized imines, isoxazoles and oxazaphospholes.[2] 2*H*-Azirines have also been prepared by the intermolecular reaction of nitriles and carbenes or nitrenes and acetylenes.[3] The most common method for preparing 2*H*-azirines however, involves the photolysis or thermolysis of vinyl azides (**1**).[4] This rearrangement can take place in a concerted manner or *via* a vinyl nitrene intermediate (**3**) (Scheme 1).[5] Pyrolysis of vinyl azides is complicated by the fact that the product.



Scheme 1

2*H*-azirines (**2**) are themselves thermally active and thus react further, decreasing the yields of formation and causing difficulty in their isolation. To avoid these problems, the Neber reaction[6] route has also been extensively utilized and can be facilitated by the incorporation of electron-withdrawing groups at the α-position of a *N*-functionalized imine (**4**) (Scheme 2). Asymmetric syntheses of 2*H*-azirines containing a carboxylic ester group[7] or a phosphorous substituent[8] by this method have been reported in recent years.

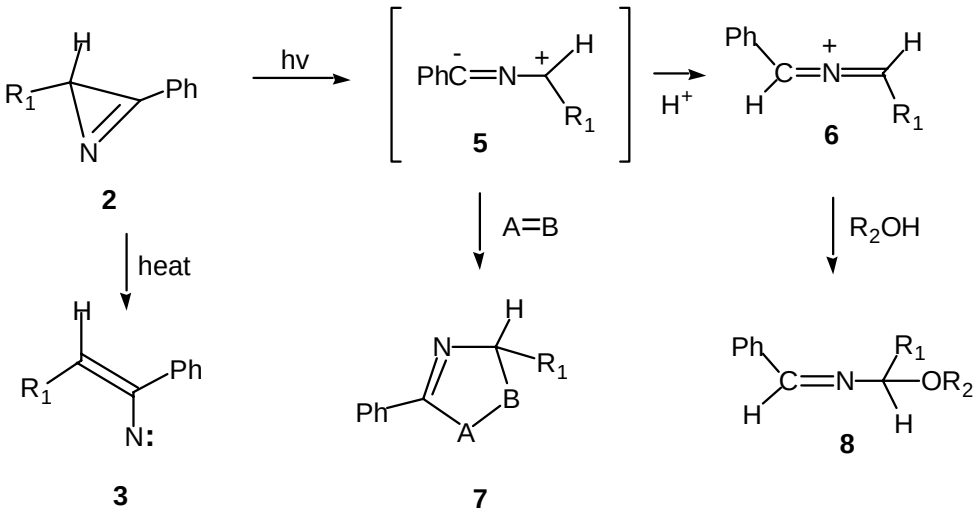


LG = Leaving group (*i.e* OTs, $N(Me)_3^+$, etc:)

Scheme 2

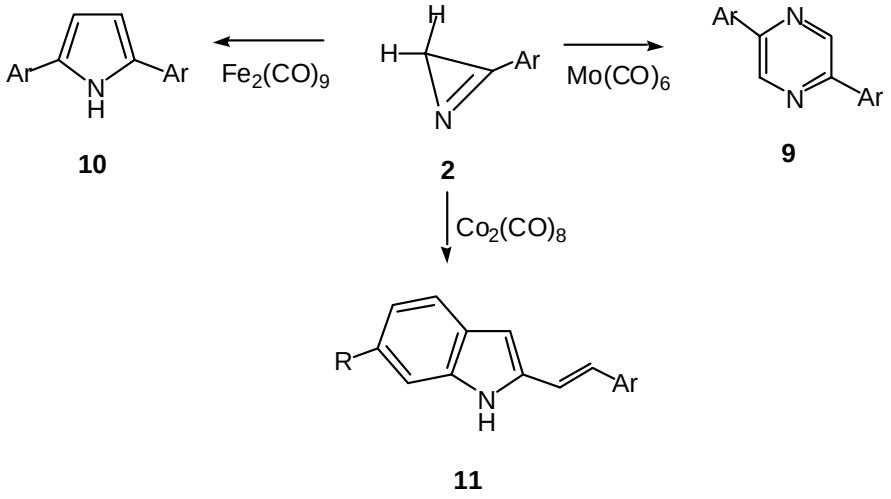
Earlier work from our laboratory demonstrated that 2*H*-azirines are photochemically active substrates.[9] Upon irradiation into their n-π*absorption bands, the strained three-membered 2*H*-azirine ring opens selectively at the C-C bond in a heterolytic fashion resulting in the formation of a nitrile ylide dipole (**5**).[9] The nitrile ylide can be trapped by alkenes or alcohols. Due to the pronounced reactivity of nitrile ylides with dipolarophiles, 2*H*-azirines have been extensively utilized in [3+2] cycloaddition reactions (Scheme 3).[10] A recent example is the facile synthesis of exohedrally functionalized fullerenes.[11] In the presence of alcohols, the photochemically

generated nitrile ylide **5** reacts to form alkoxyimines **8** and this reaction presumably proceeds by a pathway involving the intermediate production of an azaallenium cation (**6**).[12] In contrast with photochemical activation, the thermal chemistry takes place by an entirely different pathway involving rupture of the azirine C-N single bond which then produces a vinyl nitrene intermediate (**3**).[13-15]



Scheme 3

In recent years there has been considerable interest in the use of both organometallic reagents and catalysts for effecting ring cleavage of small ring systems.[16] By comparison with the extensive photochemical and thermal studies of the 2*H*-azirine ring system, its behavior toward organometallic reagents has been relatively unexplored. In some earlier work, Alper and Wollowitz[17] demonstrated that group VI metal carbonyls.



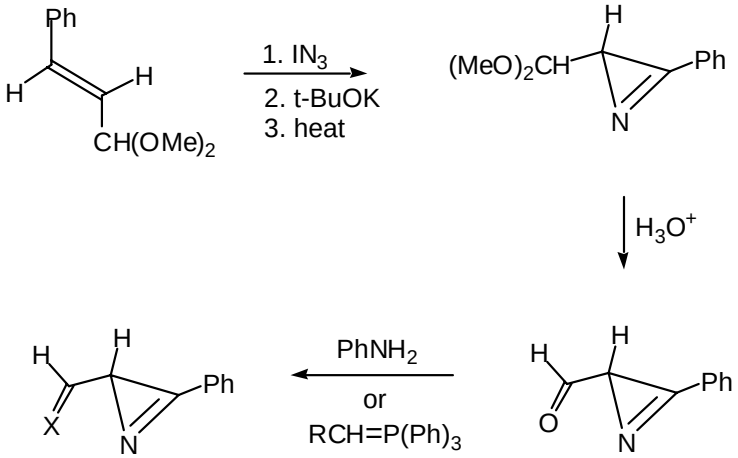
Scheme 4

$M(CO)_6$, M=Cr, Mo, W] are useful reagents for converting 2-aryl azirines to pyrazines **9**. Interestingly, pyrroles such as **10** were obtained in modest yields when diiron nonacarbonyl was employed as the organometallic reagent.[18] Mechanistic studies indicate that the formation of the pyrrole proceeds *via* carbon-nitrogen bond cleavage of the 2*H*-azirine ring. More surprisingly, treatment of the aryl substituted 2*H*-azirine with dicobalt octacarbonyl [$Co_2(CO)_8$] afforded 2-styrylindoles such as **11** in good-excellent yields (Scheme 4).[19] No mechanistic studies were carried out and the unusual chemoselectivity encountered as a function of the organometallic reagent used was not explained by the authors.

In a continuation of our own studies dealing with the chemical reactivity of 2*H*-azirines[9], we thought it would be of interest to further investigate the transition metal catalyzed reactions of several 2-phenyl-3-vinyl substituted 2*H*-azirines. In this paper we report that the commonly employed Grubbs' catalyst induces a clean rearrangement which proceeds *via* carbon-nitrogen bond cleavage of the 2*H*-azirine ring. However, when the reaction was carried out using the popular Wilkinson's catalyst [$Rh(PPh_3)_3Cl$] in an alcoholic solvent, the only product obtained in high yield corresponded to an α,β-unsaturated oxime (*vide infra*). These results provide further insight into the chemical behavior of this reactive three-membered heterocyclic ring with various transition metal catalysts.

Results and Discussion

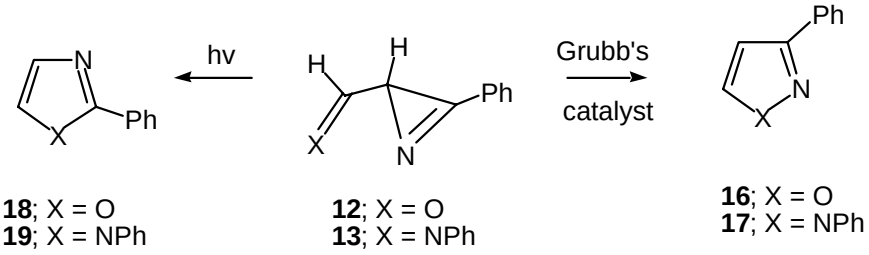
2-Formyl-3-phenyl-2*H*-azirine (**12**) was prepared by the addition of iodine azide to the dimethyl acetal of cinnamaldehyde and this was followed by dehydrohalogenation, thermolysis and aqueous hydrolysis. Further reaction of the aldehyde with aniline as well as various Wittig reagents gave the substituted 2*H*-azirines **13-15** shown in Scheme 5 in good yield.



13; X = NPh
14; X = $CHCO_2Me$ (*E*)
15; X = CHCHO (*E*)

Scheme 5

Our first transition metal catalyzed experiments centered around the use of the ruthenium 4,5-dihydroimidazo-2-ylidene complex developed by Grubbs and widely known for its application in organic and polymer synthesis.[20] To date, this catalyst is routinely used for ring closing metathesis (RCM), cross metathesis (CM), and other metathesis-type reactions. The commercial availability and effectiveness of the Grubbs' catalyst now allow olefin metathesis strategies to be viewed as practical methods for the synthesis of medium size ring,[21] spiro and polycyclic systems[22] and natural products.[23] A growing number of newly discovered catalytic processes mediated by Grubbs' carbene complex also broaden its synthetic utility beyond olefin metathesis.[24] An investigation of its chemistry with 2*H*-azirine **12** led to the discovery that it rapidly induced a rearrangement at 25 °C producing 3-phenylisoxazole (**16**) in 90% yield. Reaction of the corresponding *N*-phenylimine **13** proceeded similarly and gave 1,3-diphenylpyrazole (**17**) as the exclusive product (Scheme 6). These results stand in marked contrast to the photochemical behavior of **12** and **13** which afforded 2-phenyloxazole (**18**) and 1,2-diphenylimidazole (**19**) as the exclusive products. The photoproducts are formed by C-C bond fragmentation and subsequent cyclization of the resulting nitrile ylide.



18; X = O
19; X = NPh

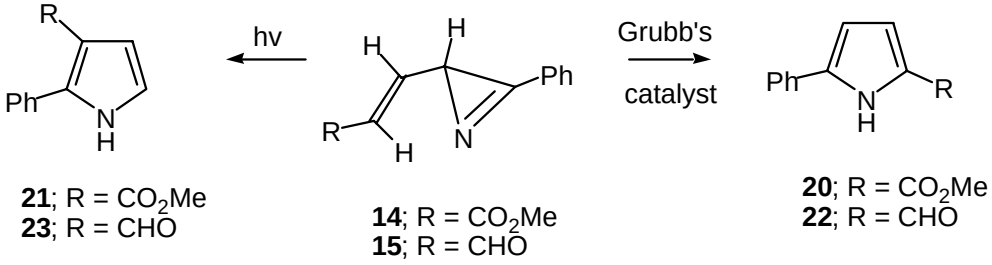
12; X = O
13; X = NPh

16; X = O
17; X = NPh

Scheme 6

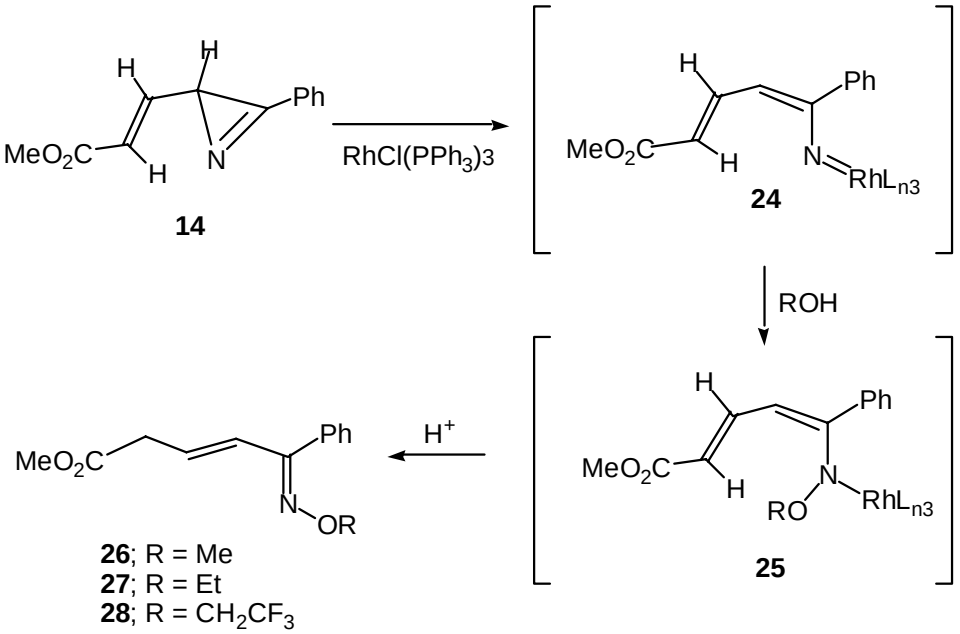
The isolation of isoxazole **16** and pyrazole **17** by use of the Grubbs' catalyst clearly indicate that these transition metal catalyzed transformations occur by C-N bond fragmentation.

Attention was next turned to the Grubbs' catalyzed reaction of methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**14**). Treatment of **14** in the presence of 5 mol% $Cl_2(Cy_3P)_2Ru{=}CHPh$ in CH_2Cl_2 at 25 °C gave 2-phenyl-5-carbomethoxypyrrole (**20**) as the exclusive product in 75% isolated yield. Photolysis of **14**, on the other hand, afforded the isomeric 2-phenyl-3-carbomethoxypyrrole (**21**) in 85% yield (Scheme 7). In an analogous manner, the reaction of the aldehydic substituted 2*H*-azirine **15** with Grubbs' catalyst furnished the 2,5-disubstituted pyrrole **22** while photolysis gave the 2,3-disubstituted pyrrole **23** in high yield. The structures of the disubstituted pyrroles were readily established by examination of their characteristic NMR spectra.



Scheme 7

Our attempts to carry out a related rearrangement using Wilkinson's catalyst [$RhCl(PPh_3)_3$] proved to be more problematic. Exposure of the 2*H*-azirinyl acrylate **14** to $RhCl(PPh_3)_3$ in CH_2Cl_2 resulted only in recovered starting material. When heated at reflux, the reaction afforded a complex mixture of products which resisted separation and purification. However, when **14** was treated with 5 mol% of Wilkinson's catalyst in methanol, a clean reaction ensued and the major product isolated in 65% yield was identified as 5-methoxyimino-5-phenyl-pent-3-enoic acid methyl ester (**26**). Similar results were obtained using ethanol and trifluoroethanol which furnished the α,β-unsaturated oximes **27** (40%) and **28** (53%). A possible mechanism for the 2*H*-azirine-$RhCl(PPh_3)_3$ reaction involves initial π-complexation of the organometallic catlyst with the imino bond. Ring opening by C-N bond cleavage would give **24** which can then react with the alcohol to afford **25**. Loss of the rhodium complex occurs upon protonation to furnish the observed product.



Scheme 8

An investigation of the reaction of variously substituted 2*H*-azirines with other commonly used transition metal catalysts is currently in progress and will be reported at a later date.

Experimental Section

General Procedures. Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70eV. Unless otherwise noted, all reactions were performed in flame dried glassware under an atmosphere of dry argon. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using an ethyl acetate/hexane mixture as the eluent unless specified otherwise. All solids were recrystallized from ethyl acetate/hexane for analytical data.

2-Formyl-3-phenyl-2*H*-azirine (12). A solution containing 8.0 g of cinnamaldehyde dimethyl acetal in 50 mL of acetonitrile was added to a suspension of iodine azide (8.5 g) in 50 mL of acetonitrile at 0 ^{o}C. The reaction mixture was allowed to stir at rt for 12 h. The resulting red-brown mixture was poured onto 50 mL of water and was extracted with ether. The combined organic extracts were washed successively with 70 mL of 5% aqueous sodium thiosulfate and 100 mL of water. The solvent was then dried over magnesium sulfate and removed under reduced pressure to give 15 g (97%) of a light yellow oil whose structure was assigned as 1-azido-3,3-dimethoxy-2-iodo-1-phenyl-propane on the basis of the following data: IR (neat) 2175 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 3.48 (s, 3H), 3.56 (s, 3H), 4.50 (1H, d, J = 4.0 Hz), 4.48 (dd, 1H, J = 9.0 and 4.0 Hz), 4.88 (1H, d, J = 9.0 Hz), and 7.52 (s, 5H).

A solution containing 15 g of 1-azido-3,3-dimethoxy-2-iodophenyl-propane in 150 mL of anhydrous ether was treated with excess potassium *tert*-butoxide (20 mol %) at -10 ^{o}C and the mixture was allowed to stir at 0 ^{o}C for an additional 5 h. The crude reaction mixture was washed twice with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residual oil was filtered through a neutral alumina column with petroleum ether to give 9.0 g of a pale yellow oil. The structure of this material was assigned as 1-azido-3,3-dimethoxy-1-phenyl-1-propene on the basis of the following data: IR (neat) 2105 and 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 3.36 (s, 6H), 4.82 (d, 1H, J = 8.0 Hz), 5.64 (d, 1H, J = 8.0 Hz), and 7.60 (s, 5H).

A solution of 9.0 g of 1-azido-3,3-dimethoxy-1-phenyl-1-propene in 100 mL of chloroform was heated at reflux for 12 h. After this time, the solvent was evaporated under reduced pressure, and the residual oil was distilled [bp 103-105 ^{o}C (0.27 mm)] to give 7.8 g of 3-phenyl-2-(dimethoxymethyl)azirine as a colorless liquid: IR (neat) 1755 cm^{1}; ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 2.42 (d, 1H, J = 3.0 Hz), 3.40 (s, 3H), 3.52 (s, 3H), 4.48 (d, 1H, J = 3.0 Hz), and 7.6-8.2 (m, 5H).

A 7.8 g sample of 3-phenyl-2-(dimethoxymethyl)azirine dissolved in 100 mL of dioxane and 150 mL of 20% aqueous acetic acid was heated at 85 ^{o}C for 45 min. The reaction mixture was rapidly cooled to 0 ^{o}C and extracted with ether. The combined organic extracts were washed

successively with 100 mL of aqueous 5% sodium bicarbonate and 100 mL of saturated sodium chloride. Removal of the solvent after drying over magnesium sulfate gave a clear oil which solidified on standing. The crystalline solid that formed (3.8 g, 55%) was collected and was sublimed at 35 ^{o}C (0.01 mm) to give white crystals of 2-formyl-3-phenyl-2*H*-azirine (**12**); mp 45-47 ^{0}C; IR (KBr) 1785 and 1710 cm^{-1}; uv (95% ethanol) 245 nm (15,500); ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 2.90 (d, 1H, J = 7.0 Hz), 7.16-7.68 (m, 5H), and 9.20 (d, 1H, J = 7.0 Hz); *m/e* 145 (base), 144, 117, 116, 90, 89, and 77; Anal. Calcd for C_9H_7NO: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.41; H, 4.91; N, 9.69.

Grubbs catalyzed rearrangement of 2-formyl-3-phenyl-2*H*-azirine (12). A solution containing 0.5 g of 2-formyl-3-phenyl-2*H*-azirine (**12**) and 0.03 g of Grubbs' catalyst in 30 mL of CH_2Cl_2 was stirred at 25 ^{o}C for 2 h. Filtration followed by removal of the solvent under reduced pressure left a dark oil which was distilled at 40 ^{o}C (0.01 mm) to give 0.4 g of 3-phenylisoxazole; IR (KBr) 3225, 2110, and 1320 cm^{-1}; *m/e* 145, 144, 89, and 77 (base); ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 6.58 (d, 1H, J = 1.5 Hz), 7.1-8.0 (m, 5H), and 8.39 (d, 1H, J = 1.5 Hz).

A solution containing 0.3 g of **12** in 50 mL of cyclohexane was irradiated through a Vycor filter sleeve for 75 min. Removal of the solvent under reduced pressure gave dark oil which was purified by chromatography on a silica gel thick layer plate using a 1:4 ethyl acetate-benzene mixture as the eluent. The clear oil obtained (0.21 g) was identical in all respects with an authentic sample of 3-phenyl)oxazole (**18**).[25]

2-Formyl-3-phenyl-2*H*-azirine-*N*-phenylimine (13). A solution of 1.4 g of azirine **12** and 0.9 g of aniline in 75 mL of benzene which contained a trace of *p*-toluene-sulfonic acid was heated at reflux for 1 h. Removal of the solvent under reduced pressure left 2.1 g of a clear oil whose structure as assigned as 2-formyl-3-phenyl-2*H*-azirine-*N*-phenylimine (**13**): IR (neat) 1785, 1640, and 1600 cm^{-1}; uv (cyclohexane) 243 nm (10,700) and 275 (4000); ^{1}H-NMR (100 MHz, $CDCl_3$) δ 3.49 (d, 1H, J = 8.0 Hz) and 7.60-8.70 (m, 11H).

Grubbs catalyzed rearrangement of 2-formyl-3-phenyl-2*H*-azirine-*N*-phenylimine (13). A solution containing 0.3 g of azirine **13** and 0.01 g of Grubbs' catalyst in 30 mL of CH_2Cl_2 was stirred at 25 ^{o}C for 3 h. Filtration followed by removal of the solvent under reduced pressure left behind an oily solid. Recrystallization of this material from 95% ethanol gave 1,3-diphenylpyrazole (**17**) in 89 % yield as a white solid, mp 84-85 ^{o}C; IR (KBr) 1590 and 1520 cm^{-1}; uv (cyclohexane) 268 nm (23,400); ^{1}H-NMR ($CDCl_3$) δ 6.86 (d, 1H, J = 2 Hz) and 7.2-8.1 (m, 11H). This material was further verified by comparison with an authentic sample.[26]

A solution containing 0.5 g of azirine **13** in 450 mL of benzene was irradiated through a Corex filter sleeve for 90 min. Removal of the solvent under reduced pressure left dark oil which was purified by thick layer chromatography. The white solid was obtained in 92 % yield and was identified as 1,2-diphenylimidazole (**19**), mp 80-81 ^{o}C; IR (KBr) 1600 cm^{-1}; uv (95% ethanol) 270 nm (16,700); *m/e* 220, 219 (base), 193, and 77; ^{1}H-NMR ($CDCl_3$) δ 7.00-5.50 (m, 12H). A picrate derivative was prepared, mp 193-194 ^{o}C; Anal Calcd for $C_{21}H_{15}N_5O_7$: C, 56.13; H, 3.36; N, 15.59. Found: C, 56.22; H, 3.47; N, 15.60.

Methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (14). A solution containing 1.4 g of 2-formyl-3-phenyl-2*H*-azirine (**12**) and 3.3 g of carbomethoxymethylenetriphenyl-phosphorane in 100 mL of benzene was heated at 50-60 °C under a nitrogen blanket for 12 h. The solution was concentrated to an oil and triturated with hexane. The precipitated triphenylphosphine oxide was filtered, and the hexane solution was concentrated under reduced pressure to give methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**14**) as a light-yellow oil in quantitative yield; IR (neat) 1770, 1730, and 1650 cm^{-1}; uv (95% ethanol) 253 and 305 nm (15,600 and 6900); ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 2.92 (d, 1H, J = 8.0 Hz), 3.72 (s, 3H), 6.20 (d, 1H, J = 16.0 Hz), 6.78 (dd, 1H, J = 16.0 and 8.0 Hz), and 7.60-8.05 (m, 5H); *m/e* 201 (base) 170, 169, 141, 140, 115, and 114; Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.45; H, 5.76; N, 6.58.

Grubbs catalyzed rearrangement of methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (14). A solution containing 0.3 g of methyl (*E*)-phenyl-2*H*-azirine-2-acrylate (**14**) and 0.01 g of Grubbs' catalyst in 30 mL of CH_2Cl_2 was stirred at 25 °C for 3 h. Filtration followed by removal of the solvent gave 2-phenyl-5-carbomethoxypyrrole (**20**) in quantitative yield: mp 142-143.5 °C; IR (KBr) 3310 and 1680 cm^{-1}; uv (95% ethanol) 220 and 317 nm (12,200 and 27,900); ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 3.84 (s, 3H), 6.60 (d, 1H, J = 4.0 Hz), 7.05 (d, 1H, J = 4.0 Hz), 7.20-7.80 (m, 5H), and 10.20 (brs, 1H); *m/e* 201, 170, 169 (base), 141, 140, 115, and 114; Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.49; H, 5.51; N, 6.86.

A solution containing 0.6 g of methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**14**) in 50 mL of benzene was irradiated through a Corex filter sleeve for 1.5 h. The solvent was removed under reduced pressure to afford dark oil. The crude oil was filtered through a silica gel column with a 10% ethyl acetate-benzene mixture to give light-orange oil which solidified on standing. Recyrstallization of the crude solid from benzene-heptane gave 2-phenyl-3-carbomethoxypyrrole (**21**) (95% ethanol) 293 nm (*e* 12,800); NMR ($CDCl_3$, 100 MHz) τ 6.32 (s, 3H), 3.24 (2H, AB quartet, J=3.0 Hz after D_2O exchange), 2.20-2.60 (m, 5H), and 0.72 (brs, 1H); *m/e* 201, 170 (base), 169, 142, 141, 140, 115, and 77.

(*E*)-3-(3-Phenyl-2*H*-azirin-2-yl)acrolein (15). A solution containing 1.3 g of 2-formyl-3-phenyl-2*H*-azirine (**12**) and 3.4 g of formylmethyltriphenylphosphorane in 100 mL of benzene was heated at 40 °C for 96 h under a nitrogen atmosphere. Removal of the solvent under reduced pressure left dark oil. This material was taken up in 20 mL of ether, and the resulting mixture was filtered to remove the triphenylphosphine oxide which had precipitated. The ethereal solution was concentrated, and the crude residue was chromatographed through a Florosil column using 10% ethyl acetate-benzene as the eluent. The yellow oil obtained was distilled at 35 °C (0.005 mm) to give 0.8 g (60%) of (*E*)-3-(3-phenyl-2*H*-azirin-2-yl)acrolein (**15**) as a clear oil: IR (KBr) 1760, 1680 and 1630 cm^{-1}; uv (95% ethanol) 256 nm (42,800) and 249 (42,500); ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 3.0 (d, 1H, J = 8.0 Hz), 6.10-6.60 (m, 2H), 7.30-8.10 (m, 5H), and 9.50 (d, 1H, J = 7.0 Hz).

Grubbs catalyzed rearrangement of (E)-3-(3-phenyl-2*H*-azirin-2-yl)-acrolein (15). A solution containing 0.1 g of azirine **15** and 0.01 g of Grubbs' catalyst in 30 mL of CH_2Cl_2 was stirred at 25 °C for 3 h. Filtration followed by removal of the solvent under reduced pressure

gave a yellow oil which solidified on standing. This material was sublimed at 60 °C (0.05 mm) to give 0.9 g of 2-phenyl-5-formylpyrrole (**22**) as a pale yellow solid: mp 137-138 °C; IR (KBr) 1650 and 1510 cm^{-1}; uv (95% ethanol) 318 nm (29,000); m/e 171 (base), 170, 116; ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 6.70 (m, 1H), 7.10 (m, 1H), 7.30-8.10 (m, 5H), 9.60 (s, 1H), and 10.40 (m, 1H); Anal. Calcd for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.01; H, 5.32; N, 8.25.

A solution containing 0.08 g of the above azirine **15** in 100 mL of hexane was irradiated at 2537 A° for 40 min. The solution was concentrated and the brown solid that formed was collected and recrystallized from benzene-hexane to give 0.07 g of 2-phenyl-3-formylpyrrole (**23**): mp 171-173°; IR (KBr) 3.16 and 6.13 μ; NMR ($CDCl_3$, 100 MHz) τ 0.08 (s, 1H), 2.18-2.76 (m, 5H), 3.02 (m, 1H), 3.32 (m, 1H), and 7.18 (NH, 1H); *m/e* 171, 170 (base), and 115.

5-Alkoxyimino-5-phenyl-pent-3-enoic acid methyl esters (26-28). In a sealed tube was placed 0.18 g (0.87 mmol) of methyl (*E*)-phenyl-2*H*-azirine-2-acrylate (**14**) in 8 mL of degassed methanol. A 0.35 g (0.038 mmol) sample of Wilkinson's catalyst was added and the reaction mixture was stirred at 70 °C for 18 h. The solvent was removed under reduced pressure and the residue was subjected to flash silica gel chromatography to give 0.13 g (62%) of 5-methoxy-imino-5-phenyl-pent-3-enoic acid methyl ester (**26**) as a colorless oil; IR (film) 2949, 1740, 1631, 1435 and 1303 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.49 (dd, 2H, J=7.0 and J=1.3 Hz), 3.69 (s, 3H), 3.88 (s, 3H), 5.17 (q, 1H, J=7.3 Hz), 6.67 (d, 1H, J=7.6 Hz), and 7.43 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 31.9, 52.0, 53.9, 114.3, 128.5, 129.0, 130.4, 131.6, 135.1, 162.1 and 173.2; Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.10; H, 6.44; N, 6.02.

In a sealed tube was placed 0.12 g (0.6 mmol) of methyl (*E*)-phenyl-2*H*-azirine-2-acrylate (**14**) in 5 mL of degassed ethanol. A 0.04 g (0.042 mmol) sample of Wilkinson's catalyst was added and the reaction mixture was stirred at 85 °C for 18 h. The solvent was removed under reduced pressure and the residue was subjected to flash silica gel chromatography to give 0.06 g (39%) of 5-ethoxy-imino-5-phenyl-pent-3-enoic acid methyl ester (**27**) as a colorless oil; IR (film) 1740, 1632, 1283 and 1163 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.37 (t, 3H, J=7.1 Hz), 3.49 (dd, 2H, J=7.0 Hz and 1.6 Hz), 3.70 (s, 3H), 4.34 (q, 2H, J=7.0 Hz), 5.16 (m, 1H), 6.67 (m, 1H), and 7.44 (m, 5H); Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.98; H, 6.93; N, 5.67. Found: C, 67.82; H, 6.91; N, 5.88.

In a sealed tube was placed 0.05 g (0.3 mmol) of methyl (*E*)-phenyl-2*H*-azirine-2-acrylate (**14**) in 5 mL of degassed trifluoroethanol. A 0.002 g (0.0016 mmol) sample of Wilkinson's catalyst was added and the reaction mixture was stirred at 90 °C for 6 h. The solvent was removed under reduced pressure and the residue was subjected to flash silica gel chromatography to give 0.04 g (53%) of 5-trifluoroethoxy-imino-5-phenyl-pent-3-enoic acid methyl ester (**28**) as a colorless oil. IR (film) 1740, 1647, 1262 and 1167 cmm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.45 (dd, 2H, J=7.0 Hz and 1.6Hz), 3.70 (s, 3H), 4.67 (q, 2H, J=8.7 Hz), 5.29 (q, 1H, J=7.0 Hz), 6.69 (dt, 1H, J=7.6 Hz and 1.6 Hz) and 7.48 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 31.9, 52.1, 62.5 (q, J=36 Hz), 116.2, 122.5, 125.2, 128.7, 129.3, 129.9, 131.2, 133.8,

159.3 and 172.8; Anal. Calcd for $C_{14}H_{14}F_3NO_3$: C, 55.82; H, 4.68, N, 4.65. Found: C, 56.02; H, 4.70; N, 4.67.

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