New Cleavage of the Azirine Ring by Single Electron Transfer: The Synthesis of 2*H*-Imidazoles, Pyridazines and Pyrrolines

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Here we report the first example of the dimerisation of azirines to 2*H*-imidazoles or 3,5-disubstituted pyridazines from a reaction promoted by $FeCl_2$. An azirine complex with a radical structure is proposed as an intermediate. Cyclopropyl ketones and pyrrolines are isolated when the reaction is carried out in the presence of styrenes.

Introduction

The cleavage of an azirine ring gives intermediates that can lead to cycloaddition reactions. It is possible to obtain reactive intermediates by cleavage of each of the three bonds of azirine.[1] Photolysis and thermolysis, as well as the use of metal carbonyls, silver salts and acids have been applied to open the azirine ring, obtaining a lot of reactive intermediates (e.g. nitrile ylides, vinyl nitrenes and various organometallic complexes.)[1]

In general, when a self-condensation occurs, the dimers obtained are derivatives of a pyrazine ring. In one case, a bromo-dimeric 2*H*-imidazole derivative from the reaction of azirine with $CuBr_2$ was obtained. Although the intermediate was isolated, no mechanism for its formation was suggested.[2]

Recently, we proved that single electron transfer is a useful way to open heterocyclic systems under very mild conditions.[3] Extending our study to azirines we found that iron dichloride is able to cleave the carbon-nitrogen single bond in the azirine ring. The radical intermediate obtained reacts with: a) another molecule of azirine to give 2*H*-imidazoles and 2,5-substituted pyridazines; b) styrene, if added as a reagent, to give new intermolecular cycloadditions with the formation of pyrrolidines.

Results and Discussion

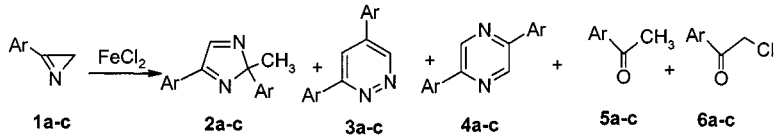
3-Aryl-2*H*-azirines (**1a−c**) were treated with anhydrous $FeCl_2$ in dry acetonitrile at room temperature for 24 h. The reaction gave 2*H*-imidazoles **2**, pyridazines **3** and pyrazines **4**, together with arylketones **5** and traces of α-chloroketones **6** (Scheme 1).

The structures of the products were elucidated by comparison with an authentic sample, or on the basis of analytical and spectral data. The molecular structure of the 2*H*-imidazole **2a** was confirmed by X-ray analysis (Figure 1).

The distribution of products and yields for **2−4** are listed in Table 1.

The reaction affords 2*H*-imidazole **2** when performed in dilute solution or pyridazine **3** in concentrated solution. These compounds were not obtained when methanol was used as the solvent, where pyrazine **4** was the only dimer present along with various unidentified compounds. When $FeCl_2 \cdot 4H_2O$ was used instead of the anhydrous salt, a decrease in the yield of 2*H*-imidazole **2** and an increase in the yield of by-products **5** and **6** was observed.

The structures of the products obtained (**2−6**) in reactions with $FeCl_2$ provide evidence that the azirine ring is cleaved at the carbon-nitrogen single bond. This cleavage can generate vinyl nitrenes as intermediates, and when it occurs, only pyrazines were produced.[1]



a: Ar = C_6H_5
b: Ar = 4F-C_6H_4
c: Ar = 4CH_3-C_6H_4

Scheme 1. Products from reaction of azirines with $FeCl_2$

It is possible that $FeCl_2$ acts as a Lewis acid to promote this ring cleavage. A reaction of azirine with $TiCl_4$ as the Lewis acid was previously reported[4] and again pyrazines were obtained. In this case a zwitterionic intermediate was

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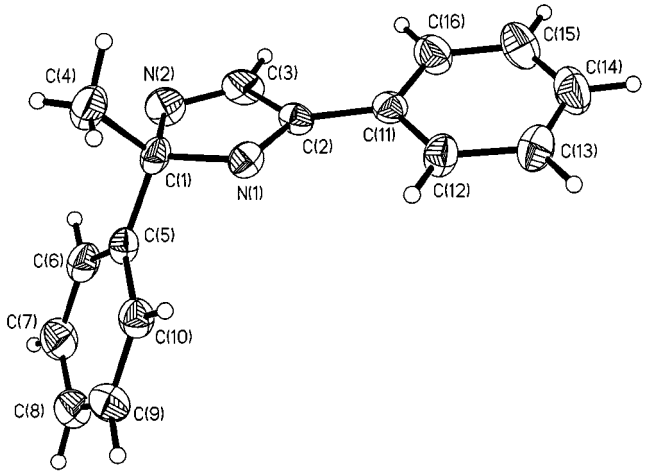


Figure 1. Molecular structure of **2a** with the atom numbering scheme; displacement ellipsoids correspond to 30% probability; H atoms are shown as spheres of arbitrary radius

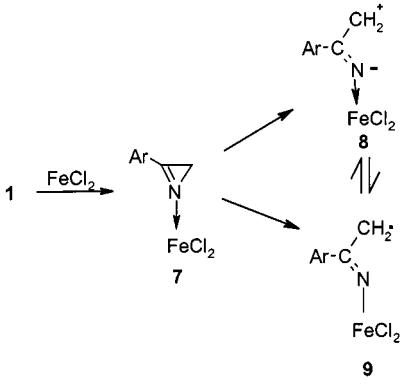
Table 1. Yields (%) of products from reaction of **1** with $FeCl_2$[a]

1	Ar	Solvent	2	3	4
a	C_6H_5	acetonitrile[b]	32	2	4
a	C_6H_5	acetonitrile[c]	5	30	traces
a	C_6H_5	methanol[c]	–	–	23
b	4F-C_6H_4	acetonitrile[b]	20	10	–
c	4CH_3-C_6H_4	acetonitrile[b]	10	26	4

[a] The reactions were performed with an equimolar amount of anhydrous $FeCl_2$ (heterogeneous phase). – [b] 0.1 M. – [c] 0.4 M.

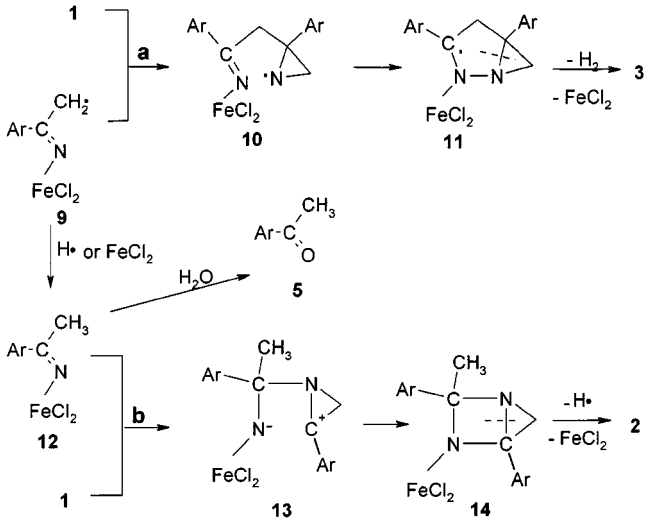
proposed. We verified the reactivity of Lewis acids towards azirines using $FeCl_3$ and $AlCl_3$. The product obtained was the pyrazine **4**, while no traces of 2*H*-imidazole **2** or pyridazine **3** were found.

We think that iron dichloride is able to induce the formation of a radical intermediate as in the reaction of isoxazoles.[3] The initial step in the azirine-$FeCl_2$ reaction is probably an *N*-donor complexation that gives intermediate **7**, followed by carbon-nitrogen cleavage to give the zwitterionic structure **8** or radical structure **9** by single electron transfer (Scheme 2).



Scheme 2. Formation of the azirine-$FeCl_2$ complex

Structure **8** could justify the formation of the by-product pyrazine **4** but not 2*H*-imidazoles **2** and pyridazines **3**. Products **2, 3** and **5** can be formed by **9**, as shown in Scheme 3.



Scheme 3. Proposed mechanism for the reaction azirine-$FeCl_2$

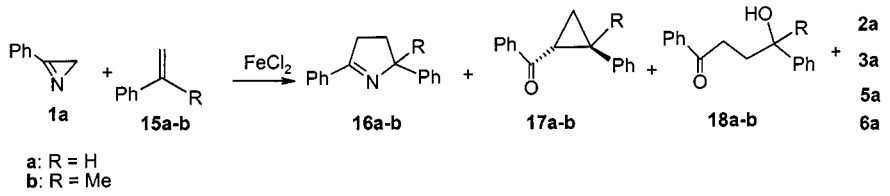
The radical structure **9** can react by routes **a** or **b**:
(a) addition to azirine **1** to give **10**, followed by cyclization to the bicyclic radical **11** which in turn gives **3** by carbon-nitrogen bond cleavage, loss of hydrogen and hydrolysis;
(b) abstraction of a hydrogen atom from the reaction medium or reduction by $FeCl_2$, to give complex **12**, followed by addition to azirine **1** to give intermediate **13** and cyclization to compound **14**, which can then afford **2** by loss of a hydrogen atom and hydrolysis. Route **b** is preferred in dilute solution, where the rate of addition between **9** and azirine becomes lower and the amount of $FeCl_2$ in solution is higher.

In order to find experimental evidence for the radical intermediate we performed the reaction in the presence of styrene or α-methylstyrene. The reaction of azirine **1a** with an excess of styrene **15a** or α-methylstyrene **15b** in the presence of iron dichloride gave pyrrolines **16**, phenyl (*trans*-2-phenylcyclopropyl) ketones **17** and hydroxy ketones **18** together with acetophenone **5a**, phenacyl chloride **6a**, 2*H*-imidazole **2a** and pyridazine **3a** (Scheme 4).

Pyrrolines **16a–b** and compounds **17b**[15] and **18b** were characterised for the first time, whereas the structures of the cyclopropyl derivative **17a** and of the hydroxy ketone **18a** were assigned by comparison with literature data. When the reaction was carried out with $FeCl_2 \cdot 4H_2O$ a large increase in the yield of hydroxy ketones **18** was obtained (Table 2).

The stereoselective formation of **17** is in agreement with a radical mechanism as the formation of cyclopropyl derivatives in radical reactions is well known.[5] Radical **9** undergoes attack by styrene to give the tautomeric intermediates **19a** and **19b** (Scheme 5).

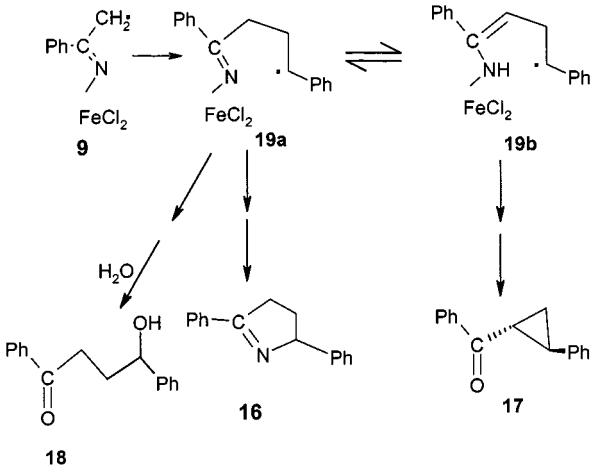
Compound **17** arises from an intramolecular reaction between the benzylic radical and the carbon-carbon double bond of the enaminic structure **19b**, while pyrroline **16** is formed from the intramolecular attack of the benzylic radical on the C=N in structure **19a**. The hydroxy ketone **18**



Scheme 4. Products from reaction of azirine **1a** with styrene and α-methylstyrene

Table 2. Yields (%) of products from the reaction of **1a** with **15a,b**

R	Promoter	16	17	18	2a	3a
H	$FeCl_2$	20	5	–	23	29
H	$FeCl_2{\cdot}4H_2O$	–	11	29	10	–
Me	$FeCl_2$	13	9	8	9	10
Me	$FeCl_2{\cdot}4H_2O$	5	5	60	traces	–



Scheme 5. Proposed mechanism for the reaction with styrene

comes from oxidation and reaction with traces of water that are in the reaction medium.

Structural Investigation

The X-ray single crystal analysis of **2a** has been carried out in order to characterise the molecular structure of the product unambiguously. A perspective view of the molecule is presented in Figure 1. It is noticeable that the racemic compound crystallises in a chiral space group with the two enantiomers coexisting as independent molecules. These molecules are correlated to each other by a noncrystallographic, and therefore approximate, centre of symmetry. The present structure is one of the few compounds containing the 2*H*-imidazole moiety reported in the Cambridge Structural Database[6] and, to the best of our knowledge, it is the first one containing the 2*H*-imidazole ring not fused with other cyclic fragments. The 2*H*-imidazole rings are planar within experimental error (r.m.s. deviation 0.003 Å) and make mean dihedral angles of 57.1(2)° and 11.6(3)° with the C5−C10 and C11−C16 phenyl rings, respectively. The C2=N1 and C3=N2 bond lengths [mean value 1.287(7) Å] are shorter than the average of 1.314(11) Å for the imidazole C=N bonds and are consistent with the $C_{arom}-C=N-C_{sp}{}^3$ sequence.[7]

Conclusion

This work has shown that iron dichloride is able to induce ring opening in an aza-heterocyclic ring by single electron transfer.[3] This new type of bond cleavage of azirines leads to a novel synthesis of 2*H*-imidazoles and pyridazines. Furthermore, the complex azirine-$FeCl_2$ could be a very interesting synthon in cycloaddition reactions as shown in the reaction with styrenes.

Experimental Section

NMR spectra were determined with TMS as internal standard on a Bruker 250 MHz instrument. MS spectra were performed with a Finnigan TSQ 70 instrument. Chromatographic separations were performed using Merck Kieselgel 60. Melting points were determined with a Kofler apparatus and are uncorrected. GLC analyses were performed with a capillary gas chromatograph equipped with a DB-5 fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness), PTV injector, flame ionisation detector, oven temperature programme 50°(1) /10°/min 160°(1) /20°/min 280°(10). The azirines were prepared from the corresponding azidostyrenes.[8] Products given as traces were detected by GLC analyses.

Reaction of 3-Phenyl-2*H*-azirine (1a) with $FeCl_2$ (0.4 M): Anhydrous iron dichloride (80 mesh; 0.635 g, 5.0 mmol) was added to a stirred degassed solution of azirine **1a** (0.58 g, 5.0 mmol) in anhydrous CH_3CN (12.5 mL) and the mixture stirred overnight. The solvent was removed, the crude product dissolved in dichloromethane and washed with an aqueous solution of HCl (0.1 M), aqueous $NaHCO_3$ and water. The residue was purified by column chromatography (eluent: *n*-hexane/ethyl acetate from 95:5 to 50:50) to give acetophenone **(5a)**, phenacyl chloride **(6a)** and 2,5-diphenylpyrazine **(4a)** in trace amounts, 2-methyl-2,4-diphenyl-2*H*-imidazole (**2a**; 0.030 g, 5%), and 3,5-diphenylpyridazine (**3a**; 0.125 g, 30%).[10]

2-Methyl-2,4-diphenyl-2*H*-imidazole (2a): Needles, m.p. (*n*-hexane) 89−91 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.85 (s, 3 H), 7.20−7.40 (m, 3 H), 7.44−7.58 (m, 3 H), 7.66−7.76 (m, 2 H), 8.00−8.10 (m, 2 H), 8.47 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 27.0, 109.1, 126.9, 127.7, 128.3, 129.1, 131.1, 131.5, 140.1, 154.4, 163.8. − MS: *m*/*z* (%) = 234 (92) [M^+] 207 (100), 206 (40). − $C_{16}H_{14}N_2$ (234.3): calcd. C 82.02, H 6.02, N 11.96; found C 82.11, H 6.05, N 11.89.

3,5-Diphenylpyridazine (3a):[9] ^{1}H NMR ($CDCl_3$): δ = 7.45−7.64 (m, 6 H), 7.66−7.78 (m, 2 H), 7.98 (d, *J* = 2 Hz, 1 H), 8.08−8.20 (m, 2 H), 9.40 (s, 1 H).

Reaction of 3-Phenyl-2*H*-azirine (1a) with $FeCl_2$ (0.1 M): The same procedure as above was used but with 50 mL of solvent. Aceto-

phenone **(5a)** and phenacyl chloride **(6a)** were obtained in trace amounts along with 2,5-diphenylpyrazine (**4a**; 0.024 g, 4%),[10] 2-methyl-2,4-diphenyl-2*H*-imidazole (**2a**; 0.19 g, 32%) and 3,5-diphenylpyridazine (**3a**; 0.012 g, 2%).

Reaction of 3-(4-Fluorophenyl)-2*H*-azirine (1b) with $FeCl_2$: Anhydrous iron dichloride (80 mesh; 0.51 g, 4 mmol) was added to a stirred, degassed solution of azirine **1b** (0.50 g, 3.7 mmol) in anhydrous CH_3CN (37 mL), and the mixture stirred overnight. The solvent was removed, the crude product dissolved in dichloromethane and washed with an aqueous solution of HCl (0.1 M), aqueous $NaHCO_3$ and water. The residue was purified by column chromatography (eluent: *n*-hexane/ethyl acetate from 95:5 to 50:50) to give 4-fluoroacetophenone **(5b)** in traces, 2,4-bis(4-fluorophenyl)-2-methyl-2*H*-imidazole (**2b**; 0.10 g; 20%) and 3,5-bis(4-fluorophenyl)pyridazine **(3b**; 0.05 g, 10%).

2,4-Bis(4-fluorophenyl)-2-methyl-2*H*-imidazole (2b): Colourless solid m.p. (*n*-hexane) 100−103 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.80 (s, 3 H), 6.95−7.08 (m, 2 H), 7.14−7.28 (m, 2 H), 7.60−7.76 (m, 2 H), 8.00−8.12 (m, 2 H), 8.43 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 27.2, 108.7, 115.1 (d, *J* = 20 Hz), 116.3 (d, *J* = 22 Hz), 127.2 (d, *J* = 4 Hz), 128.7 (d, *J* = 7 Hz), 130.5 (d, *J* = 7 Hz), 135.9 (d, *J* = 4 Hz), 154.1, 162.2 (d, *J* = 246 Hz), 162.7, 164.8 (d, *J* = 252 Hz). − MS: *m*/*z* (%) = 270 (80) [M^+], 243 (96), 242 (26), 122 (100), 121 (71), 107 (28), 101 (34), 96 (47), 94 (25). − $C_{16}H_{12}F_2N_2$ (270.3): calcd. C 71.10, H 4.48, N 10.36; found C 71.18, H 4.53, N 10.25.

3,5-Bis(4-fluorophenyl)pyridazine (3b): M.p. (MeOH) 220−224 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.16−7.36 (m, 4 H), 7.64−7.80 (m, 2 H), 7.92 (d, *J* = 2 Hz, 1 H), 8.04−8.20 (m, 2 H), 9.35 (s, 1 H). − MS: *m*/*z* (%) = 268 (100) [M^+], 120 (12). − $C_{16}H_{10}F_2N_2$ (268.3): calcd. C 71.64, H 3.76, N 10.44; found C 71.73, H 3.81, N 10.37.

Reaction of 3-(*p*-Tolylphenyl)-2*H*-azirine (1c) with $FeCl_2$: Anhydrous iron dichloride (80 mesh; 0.49 g, 3.8 mmol) was added to a stirred degassed solution of azirine **1c** (0.50 g, 3.8 mmol) in anhydrous CH_3CN (38 mL) and the mixture stirred overnight. The solvent was removed, the crude product dissolved in dichloromethane and washed with an aqueous solution of HCl (0.1 M), aqueous $NaHCO_3$ and water. The residue was purified by column chromatography (eluent: *n*-hexane/ethyl acetate from 95:5 to 50:50) to give 4-methylacetophenone **(5c)** in trace amounts, 2,5-di-*p*-tolyl-pyrazine[11] (**4c**; 0.02 g, 4%), 2-methyl-2,4-di-*p*-tolyl-2*H*-imidazole (**2c**; 0.05 g, 10%) and 3,5-di-*p*-tolylpyridazine (**3c**; 0.13 g, 26%).

2-Methyl-2,4-di-*p*-tolyl-2*H*-imidazole (2c): Viscous oil − ^{1}H NMR ($CDCl_3$): δ = 1.82 (s, 3 H), 2.32 (s, 3 H), 2.42 (s, 3 H), 7.15 (d, *J* = 8 Hz, 2 H), 7.30 (d, *J* = 8 Hz, 2 H), 7.58 (d, *J* = 8 Hz, 2 H), 7.94 (d, *J* = 8 Hz, 2 H), 8.43 (s, 1 H) − ^{13}C NMR ($CDCl_3$): δ = 21.0, 21.6, 26.9, 108.9, 126.8, 128.3, 129.0, 129.7, 137.3, 137.4, 141.8, 154.3, 163.6. − MS: *m*/*z* (%) = 263 (23) [M^+ + 1], 262 (100) [M^+], 235 (75).

3,5-Di-*p*-tolylpyridazine (3c): White solid, m.p. (*n*-hexane/AcOEt) 201−204 °C (ref.[12] 199−200 °C) − ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 6 H), 7.36 (d, *J* = 8 Hz, 2 H), 7.37 (d, *J* = 8 Hz, 2 H), 7.64 (d, *J* = 8 Hz, 2 H), 7.96 (d, *J* = 2 Hz, 2 H), 8.04 (d, *J* = 8 Hz, 2 H), 9.37 (d, *J* = 2 Hz, 1 H) − ^{13}C NMR ($CDCl_3$): δ = 21.3, 21.4, 120.5, 127.0, 127.1, 129.8, 130.3, 131.9, 133.6, 139.0, 140.3, 140.4, 148.1, 159.3.

Reaction of 3-Phenyl-2*H*-azirine (1a) with Styrene in the Presence of $FeCl_2$: To a stirred degassed mixture of styrene (15 mL, 131 mmol) and anhydrous iron dichloride (3.56 g, 28 mmol) in anhydrous CH_3CN (15 mL) kept at 45 °C was added dropwise phenylazirine **1a** (3.00 g, 26 mmol) in CH_3CN (7 mL) at a rate of 2 mL h^{-1}, and the mixture stirred overnight. The solvent was removed, the crude product dissolved in dichloromethane and washed with an aqueous solution of HCl (0.1 M), aqueous $NaHCO_3$ and water. The residue was purified by column chromatography (eluent: *n*-hexane/ethyl acetate from 95:5 to 50:50) to give phenyl-(*trans*-2-phenylcyclopropyl)methanone **(17a**; 0.27 g, 5%), acetophenone (**5a**; 0.12 g, 4%), 2,5-diphenylpyrroline (**16a**; 1.15 g, 20%), 2-methyl-2,4-diphenyl-2*H*-imidazole (**2a**; 0.68 g, 23%) and 3,5-diphenylpyridazine (**3a**; 0.86 g, 29%).

Phenyl-(*trans*-2-phenylcyclopropyl)methanone (17a):[13a][13b] Oil. − ^{1}H NMR ($CDCl_3$): δ = 1.55 (m, 1 H), 1.92 (m, 1 H), 2.70 (m, 1 H), 2.90 (m, 1 H), 7.10−7.60 (m, 8 H), 7.99 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 19.2, 29.2, 29.9, 126.1, 126.5, 128.0, 128.5, 132.8, 137.6, 140.4, 198.4.

2,5-Diphenylpyrroline (16a): Oil. − ^{1}H NMR ($CDCl_3$): δ = 1.89 (m, 1 H), 2.59 (m, 1 H), 2.90−3.30 (m, 2 H), 5.31 (m, 1 H), 7.18−7.50 (m, 8 H), 7.95 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 32.3, 35.4, 75.8, 126.4, 126.7, 127.8, 128.3, 130.5, 134.3, 144.4, 173.6. − MS: *m*/*z* = 221 (49) [M^+], 220 (35), 193 (71), 192 (32), 165 (25), 118 (31), 117 (69), 115 (51), 89 (100).

Reaction of 3-Phenyl-2*H*-azirine (1a) with Styrene in the Presence of Hydrated $FeCl_2$: To a stirred degassed mixture of styrene (15 mL, 131 mmol), and anhydrous iron dichloride (5.60 g, 28 mmol) in CH_3CN (15 mL) kept at 45 °C, was added dropwise phenylazirine **1a** (3.00 g, 26 mmol) in CH_3CN (7 mL) at a rate of 2 mL h^{-1}, and the mixture stirred overnight. The solvent was removed, the crude product dissolved in dichloromethane and washed with an aqueous solution of HCl (0.1 M), aqueous $NaHCO_3$ and water. The residue was purified by column chromatography (eluent: *n*-hexane/ethyl acetate form 95:5 to 50:50) to give phenyl-(*trans*-2-methyl-2-phenyl-cyclopropyl)methanone **(17a**; 0.63 g, 11%), acetophenone (**5a**; 0.39 g, 13%), a 2:1 mixture (0.50 g) of acetophenone **(5a)** and phenacyl chloride **(6a)**, 2-methyl-2,4-diphenyl-2*H*-imidazole (**2a**; 0.30 g, 10%), and 4-hydroxy-1,4-diphenyl-butan-1-one (**18a**; 1.80 g, 29%).

4-Hydroxy-1,4-diphenylbutan-1-one (18a):[14a] M.p. 93−94 °C, (ref.[14b] 95 °C). − ^{1}H NMR ($CDCl_3$): δ = 2.20 (m, 2 H), 3.11 (t, *J* = 7 Hz, 2 H), 4.83 (m, 1 H), 7.20−7.60 (m, 8 H), 7.94 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 33.0, 34.6, 73.3, 125.7, 127.4, 128.0, 128.3, 128.4, 133.0, 136.7, 144.3, 200.5.

Reaction of 3-Phenyl-2*H*-azirine (1a) with α-Methylstyrene in the Presence of Anhydrous $FeCl_2$: To a stirred degassed mixture of α-methylstyrene (11 mL, 85 mmol), and anhydrous iron dichloride (2.40 g, 19 mmol) in anhydrous CH_3CN (7 mL) kept at 45 °C, was added dropwise phenylazirine **1a** (2.00 g, 17 mmol) in CH_3CN (8 mL) at a rate of 2 mL h^{-1}, and the mixture stirred overnight. The solvent was removed, the crude product dissolved in dichloromethane and washed with an aqueous solution of HCl (0.1 M), aqueous $NaHCO_3$ and water. The residue was purified by column chromatography (eluent: *n*-hexane/ethyl acetate from 95:5 to 50:50) to give phenyl-(*trans*-2-methyl-2-phenyl-cyclopropyl)methanone[15] (**17b**; 0.38 g, 9%), 2-methyl-2,5-diphenylpyrroline (**16b**; 0.52 g, 13%), acetophenone (**5a**; 0.36 g, 17%), 2-methyl-2,4-diphenyl-2*H*-imidazole (**2a**; 0.18 g, 9%), 3,5-diphenyl-pyridazine (**3a**; 0.21 g, 10%) and 4-hydroxy-4-methyl-1,4-diphenylbutan-1-one (**18b**; 0.34 g, 8%).

Phenyl(*trans*-2-methyl-2-phenylcyclopropyl)methanone (17b):[15] Oil. − ^{1}H NMR ($CDCl_3$): δ = 1.44 (s, 3 H), 1.61 (dd, *J* = 5 and 8 Hz, 1 H), 1.88 (dd, *J* = 5 and 6 Hz, 1 H), 2.91 (dd, *J* = 6 and 8 Hz, 1 H), 7.20−7.60 (m, 8 H), 7.99 (m, 2 H).

2-Methyl-2,5-diphenylpyrroline (16b): Oil. − ^{1}H NMR ($CDCl_3$): δ = 1.64 (s, 3 H), 2.25 (m, 2 H), 2.85−3.20 (m, 2 H), 7.10−7.60 (m, 8 H), 7.95 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 29.5, 35.0, 38.0, 78.1, 125.2, 126.1, 127.8, 128.1, 128.4, 130.4, 134.6, 149.1, 171.1 − MS: *m*/*z* (%) = 235 (11) [M^+], 220 (110), 207 (51), 206 (59), 131 (26), 117 (38), 115 (68).

4-Hydroxy-4-methyl-1,4-diphenylbutan-1-one (18b): Oil − ^{1}H NMR ($CDCl_3$): δ = 1.58 (s, 3 H), 2.25 (m, 2 H), 2.70−3.20 (m, 2 H), 7.10−7.55 (m, 8 H), 7.82 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 31.0, 33.6, 37.6, 73.8, 124.7, 126.4, 127.9, 128.1, 128.3, 132.9, 136.7, 147.1, 201.1 − MS: *m*/*z* (%) = 254 (1) [M^+], 237 (100), 134 (27), 133 (30), 121 (36), 105 (33).

Reaction of 3-Phenyl-2*H*-azirine (1a) with α-Methylstyrene in the Presence of Hydrated $FeCl_2$: To a stirred degassed mixture of α-methylstyrene (17 mL, 130 mmol), and hydrated iron dichloride (5.8 g, 29 mmol) in CH_3CN (15 mL) kept at 45 °C, was added dropwise phenylazirine **1a** (3.00 g, 26 mmol) in CH_3CN (7 mL) at a rate of 2 mL h^{-1}, and the mixture stirred overnight. The solvent was removed, the crude product dissolved in dichloromethane and washed with an aqueous solution of HCl (0.1 M), aqueous $NaHCO_3$ and water. The residue was purified by column chromatography (eluent: *n*-hexane/ethyl acetate) to give phenyl-(*trans*-2-methyl-2-phenylcyclopropyl)methanone (**17b**; 0.32 g, 5%), 2-methyl-2,5-diphenylpyrroline (**16b**; 0.32 g, 5%), acetophenone (**5a**; 0.37 g, 12%), a 2:1 mixture (0.26 g) of acetophenone **(5a)** and phenacyl chloride **(6a)**, traces of 2-methyl-2,4-diphenyl-2*H*-imidazole **(2a)**, and 4-hydroxy-4-methyl-1,4-diphenylbutan-1-one (**18b**; 3.85 g, 60%).

Crystal Structure Analysis of 2a:[18] $C_{16}H_{14}N_2$, M_r = 234.3, orthorhombic, space group $P2_12_12_1$, a = 5.713(1), b = 16.058(2), c = 27.966(4) Å, V = 2565.4(7) Å^3, Z = 8 (two crystallographically independent molecules in the unit cell), D_c = 1.21 gcm^{-3}, μ = 0.559 mm^{-1}, F(000) = 992; λ = 1.54179 Å, room temperature. A colourless crystal, suitable for X-ray analysis, with a platelet form and approximate dimensions of 0.2 × 0.3 × 0.05 mm was obtained by crystallisation from *n*-hexane. Intensity data were collected on a Siemens P4 diffractometer with graphite monochromated Cu-K_α radiation (λ = 1.54179A°), using the θ/2θ scan technique. Unit cell parameters were determined from 53 reflections in the range 16 ≤ 2θ ≤ 46°; a total of 3190 reflections (2967 unique, R_{int} = 0.046) were collected up to 130° in 2θ, with completeness to 2θ of 92.8% and index range: $-1 \le h \ge 6$, $-1 \le k \ge 18$, $-1 \le l \ge 32$. A correction for Lorentz and polarisation effects was applied; no decay correction was deemed necessary.

The structure was solved by direct methods using the SIR97 program,[16] which revealed the position of all non-H atoms; all H atoms were added at ideal calculated positions and refined using a riding model. Because of the quite low reflection-to-parameter ratio, due to the presence of two independent molecules in the unit cell, the refinement, based on F^2, was carried out separately on each molecule by blocked full-matrix least-squares procedure, with SHELXL-97.[17] In each cycle of refinement, with anisotropic temperature factors for all non-H atoms, 168 parameters were refined. The final stage of refinement converged to R = 0.059 for 1615 observed reflections, with $I \ge 2\sigma(I)$, and R = 0.139 for all data. The mean shift/error was 0.005 and the goodness of fit, S, was 0.990. The final difference map showed a maximum and minimum residual peaks of 0.16 and −0.18 e Å^{-3}, respectively.

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