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# Reactions of 2*H*-azirines with carbenoids from diazo esters: transformations of novel azirinium ylides

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**Abstract**—Thermocatalytic decomposition of diazo esters in the presence of 3-aryl-2*H*-azirines gives rise to azirinium ylides. The latter preferentially transform via isomerization into 2-azabuta-1,3-diene derivatives or, with excess diazo compound, via reaction with the Rh-carbenoid to form 3,4-dihydro-2*H*-pyrrole derivatives. In contrast, ylides generated from 2-monosubstituted or 2,2-disubstituted 3-phenyl-2*H*-azirines transform exclusively via isomerization into the corresponding 2-azabuta-1,3-dienes in high yields.


Progress in carbene chemistry has resulted in the development of synthetic approaches that employ ylides generated by carbene and carbenoid reactions with heteroatomic molecules as synthetic building blocks.[1] Carbene reactions provide ylides unavailable by traditional methods. Specifically, over the last few years much emphasis has been placed on reactions of difluoro-,[1,2] dichloro-,[1,3] and arylhalocarbenes[4] and metallocarbenoids from diazo compounds[5] with C=N compounds, which yield iminium ylides. The structural features of 2*H*-azirines, in particular, the presence of highly strained C=N bonds, make these compounds very reactive and thus quite promising synthetically.[6] Although the chemistry of 2*H*-azirines has attracted considerable interest, their reactions with electrophilic carbenes, leading to the formation of unusual strained azomethine ylides, have scarcely been studied.

Hassner et al. have shown that the reactions of dichlorocarbene with 2*H*-azirines involve the opening of the three-membered ring to form *N*-vinyl-*N*-dichloromethyleneamines, presumably through the corresponding azirinium dichloromethanides and subsequent rearrangement of the latter, directly or through cyclization, into transient 1-azabicyclobutanes.[7] Later, we were able to detect the formation of fluorine-containing azirinium ylides in the reactions of 2*H*-azirines with difluorocarbene, by effecting their 1,3-dipolar cycloaddition to dimethyl acetylenedicarboxylate and benzaldehyde.[8]

It was found that diazomethane and phenyldiazomethane react with 2*H*-azirines to provide the corresponding vinyl azides.[9] The latter probably result from ring opening in the adduct formed by 1,3-dipolar cycloaddition of the diazo compound to the azirine C=N bond.[9] The reaction of diphenyldiazomethane with 2,3-diphenyl-2*H*-azirine in boiling toluene gives rise to *N*-benzhydryl-*N*-(1,3,3-triphenylallylidene)amine, *N*-benzhydrylidene-*N*-(1,3,3-triphenylpropenyl)amine, and 2,3,5-triphenyl-3,4-dihydro-2*H*-pyrrole, which can be considered as 1:2-adducts of the azirine and the diphenylcarbene formed by thermal decomposition of the diazo compound.[10] Reactions of azirines with carbenoids generated by catalytic decomposition of diazo compounds are unexplored.

We have studied reactions of azirinium ylides formed from 2*H*-azirines and rhodium carbenoids generated by thermocatalytic decomposition of α-diazo esters in the presence of 1–3 mol% dirhodium tetraacetate in boiling methylene chloride (methyl phenyldiazoacetate **1**) or chloroform (dimethyl diazomalonate **2**).

All the newly obtained compounds were fully characterized using standard spectral and analytical methods.[11]

*Keywords*: Azirines; Strained azomethine ylides; α-Diazo esters; Carbenoids; 2-Azabuta-1,4-dienes; Pyrrolines.
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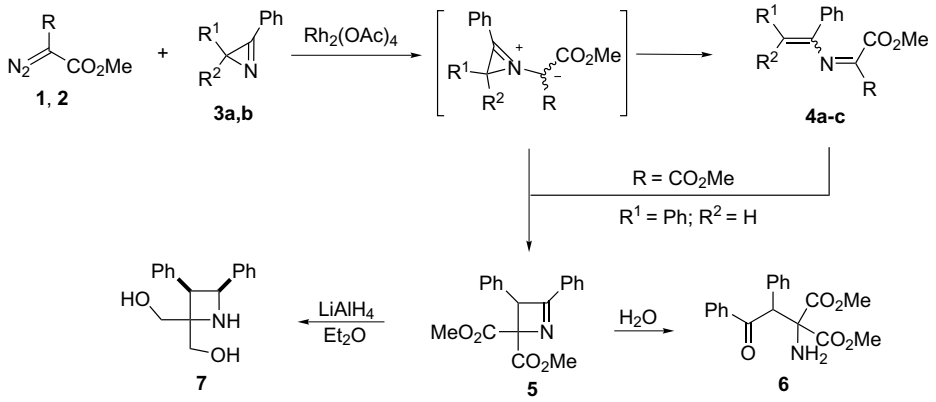



**Scheme 1.**

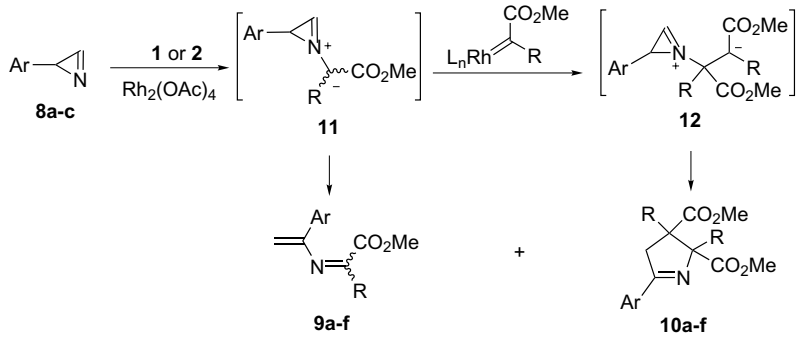
**Table 1.** Reactions of azirines **3a**,**b** with diazo esters **1**, **2**

| Azirine | Diazo ester | R | $R^1$ | $R^2$ | Solvent | Temperature (°C) | Product | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| **3a** | **1** | Ph | Ph | H | $CH_2Cl_2$ | 40 | **4a** | 68 |
| **3a** | **2** | $CO_2Me$ | Ph | H | $CHCl_3$ | 61 | **5** | 73 |
| **3b** | **1** | Ph | Biphenyl-2,2′-diyl | | $CH_2Cl_2$ | 40 | **4b** | 86 |
| **3b** | **2** | $CO_2Me$ | Biphenyl-2,2′-diyl | | $CHCl_3$ | 61 | **4c** | 80 |

The reactions of azirines **3a**,**b** with diazo ester **1** and of azirine **3b** with diazo ester **2** in the presence of catalytic amounts of $Rh_2(OAc)_4$ gave azadienes **4a**–**c** (**4a**,**b** as a single stereoisomer) in good yields (Scheme 1, Table 1). Azadienes **4a**–**c** are stable compounds, withstanding chromatography and handling at −20 °C for several months.

Unexpectedly, under the same conditions, the reaction of azirine **3a** with diazomalonate **2** afforded azetine **5** in 73% yield. The expected azadiene of type **4** was not detected in the reaction mixture. Upon standing at room temperature in a hexane–ethyl acetate solution, compound **5** was hydrolyzed quantitatively to malonate **6**. The structure of azetine **5** was proved by spectral data and by reduction to diol **7** under the action of $LiAlH_4$. Azetine **5** probably results from cyclization of the corresponding azadiene or azirinium ylide. The lack of such a reaction in the other cases can be explained by both steric and electronic reasons. For example, the $PhC^+H–CPh{=}N–C^-(CO_2Me)_2$ polarization facilitating cyclization should be appreciable only with the azadiene $PhCH{=}CPh–N{=}C(CO_2Me)_2$, since it has two strongly accepting $CO_2Me$ substituents to stabilize the negative charge and a Ph substituent to stabilize the positive charge.

The chemical behavior of 2-unsubstituted 3-aryl-2*H*-azirines **8a**–**c** under the conditions of the thermocatalytic decomposition of diazo compounds **1** and **2** established that the intermediate azirinium ylide is stabilized in a more complicated fashion as compared with ylides from 2-substituted 3-aryl-2*H*-azirines. Thus, refluxing a mixture of azirines **8a**–**c** and diazoacetate **1** in the presence of catalytic amounts of $Rh_2(OAc)_4$ in $CH_2Cl_2$ gave, along with azadienes **9a**–**c**, stereoisomeric pyrrolines **10a**–**c** (*cis*:*trans* ratio 2.3–1.5:1). The reaction of azirines **8a**–**c** with diazomalonate **2**, also, resulted in the preparation of the corresponding azadienes (**9d**–**f**) and pyrrolines (**10d**–**f**) (Scheme 2, Table 2).




**Scheme 2.**

**Table 2.** Reactions of azirines **8a–c** with diazo esters **1**, **2**

| Azirine | Diazo ester | Ar | R | Ratio **8**:**1** or **2** | Products (yield, %) |
|---|---|---|---|---|---|
| **8a** | **1** | 4-$MeC_6H_4$ | Ph | 1:1.93 | **9a** (56), **10a** (20) |
| **8a** | **1** | 4-$MeC_6H_4$ | Ph | 1:3.72 | **9a** (23), **10a** (45) |
| **8a** | **1** | 4-$MeC_6H_4$ | Ph | 1:6.02 | **9a** (9), **10a** (60) |
| **8b** | **1** | Ph | Ph | 1:2.00 | **9b** (56), **10b** (10) |
| **8c** | **1** | 4-$BrC_6H_4$ | Ph | 1:2.23 | **9c** (62), **10c** (18) |
| **8a** | **2** | 4-$MeC_6H_4$ | $CO_2Me$ | 1:1.21 | **9d** (52), **10d** (19) |
| **8b** | **2** | Ph | $CO_2Me$ | 1:1.13 | **9e** (51), **10e** (17) |
| **8b** | **2** | 4-$BrC_6H_4$ | $CO_2Me$ | 1:1.24 | **9f** (43), **10f** (31) |

Taking into account that the product ratio in the reaction of 3-aryl-substituted azirines **8a–c** with diazo compound **1** (azadiene **9** and pyrrolines **10**) is strongly dependent on the azirine:diazo compound ratio, as well as on the lack of the azadiene → pyrroline transformation under the reaction conditions, we can propose the following pyrroline formation pathway (Scheme 2). The carbenoid generated from the diazo compound and Rh-catalyst may react with the azirine **8** to yield the azirinium ylide **11**, which opens to give azadiene **9**. The reaction of ylide **11** with the electrophilic carbenoid may also provide betaine **12**, which in the case of 2-unsubstituted 2*H*-azirines, undergoes isomerization forming the pyrroline. 2-Substituents in the 2*H*-azirine prevent such recyclization and the betaine can cleave to give the starting azirine and the 'carbene dimer'. Therefore, the transformation of ylide into azadiene is the preferred reaction pathway of 2-substituted 2*H*-azirines **3a**,**b**.

The ylides **11** generated by reactions of 3-aryl-2*H*-azirines with rhodium carbenoids, unlike fluorine-containing azirinium ylides,[8] could not be trapped by means of 1,3-dipolar cycloaddition reactions, probably because of steric effects (Ph and $CO_2Me$ are bulkier than F).

Thus, methoxycarbonyl(phenyl)- and dimethoxycarbonyl-substituted azirinium ylides from 2-unsubstituted 3-aryl-2*H*-azirines are preferentially converted via isomerization into 2-azabuta-1,3-diene derivatives or, with excess diazo compound, via reaction with the carbenoid into 3,4-dihydro-2*H*-pyrrole derivatives, whereas ylides generated from 2-monosubstituted and 2,2-disubstituted 2*H*-azirine rearrange exclusively into the corresponding 2-azabuta-1,3-dienes in high yields.

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11. Data for selected compounds: **4a** mp 95–97 °C (hexane–AcOEt); IR $\nu_{max}$ ($CHCl_3$): 1745 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): 3.88 (s, 3H, MeO), 6.14 (s, 1H,=CH), 7.10–7.16 (m, 5H, H(Ph)), 7.34–7.50 (m, 8H, H(Ph)), 7.87–7.90 (m, 2H, H(Ph)); $^{13}C$ NMR (75 MHz, $CDCl_3$): 51.6 (MeO), 113.2 (=CH), 126.2, 127.7, 127.9, 128.0, 128.3, 128.9, 129.1, 131.4, 133.2, 135.6, 135.9 C(Ph), 150.3 (=C), 157.6 (C=N), 165.2 (C=O). Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.99; H, 5.75; N, 4.11; **4b** mp 150 °C (hexane); UV $\lambda_{max}$/nm (log $\varepsilon$) (hexane): 329 (4.18), 405 (3.79); IR $\nu_{max}$ ($CHCl_3$): 1750 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): 3.61 (br s, 3H, MeO), 6.65–6.68 (m, 1H, H(Ar)), 6.92–6.95 (m, 1H, H(Ar)), 7.22–7.27 (m, 2H, H(Ar)), 7.35–7.38 (m, 1H, H(Ar)), 7.48–7.55 (m, 8H, H(Ar)), 7.74–7.92 (m, 5H, H(Ar)); $^{13}C$ NMR (75 MHz, $CDCl_3$): 51.86 (MeO), 118.9 $C^2$, 119.1, 122.9, 123.4, 125.9, 126.1, 126.6, 126.7, 126.8, 128.1, 128.3, 128.5, 128.8, 129.8, 131.7, 133.5, 137.3, 137.4, 137.6, 139.1, 139.8 C(Ar), 147.6 (=CN), 159.3 (C=N), 164.4 (C=O). Anal. Calcd for $C_{29}H_{21}NO_4$: C, 83.83; H, 5.09; N, 3.37. Found: C, 83.92; H, 5.20; N, 3.37; **5**, oil, IR $\nu_{max}$ ($CHCl_3$): 1750 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): 3.33 (s, 3H, MeO), 3.89 (s, 3H, MeO), 5.44 (s, 1H, H(3)), 7.18–7.22 (m, 2H, H(Ph)), 7.27–7.31 (m, 3H, H(Ph)), 7.38–7.44 (m, 2H, H(Ph)), 7.50–7.55 (m, 1H, H(Ph)), 7.73–7.76 (m, 2H, H(Ph)); $^{13}C$ NMR (75 MHz, $CDCl_3$): 51.8 (MeO), 53.0 (MeO), 55.0 $C^3$, 77.0 $C^2$, 126.5, 127.8, 128.2, 128.3, 128.4, 130.4, 132.4, 138.8 C(Ph), 166.0 (C=O), 167.4 (C=O), 190.4 (C=N); Mass-spectrum (EI, 70 eV), $m/z$ ($I_m$, %): 323 ([$M^+$], 23), 264 ([$M^+$–$CO_2Me$], 75), 204 ([$M^+$–$CO_2Me$–$MeCO_2H$], 100), 188 (28), 178 (83), 105 (56), 77 (53); **6**, mp 160 °C (hexane–AcOEt); IR $\nu_{max}$ ($CHCl_3$): 3400, 3330, 1750 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): 2.62 (br s, 2H, $NH_2$), 3.74 (s, 3H, MeO), 3.76 (s, 3H, MeO), 5.72 (s, 1H), 7.29–7.38 (m, 7H, H(Ph)), 7.43–7.49 (m, 1H, H(Ph)), 7.88–7.91 (m, 2H, H(Ph)); $^{13}C$ NMR (75 MHz, $CDCl_3$): 52.8 (MeO), 53.0 (MeO), 56.7 (CH), 69.8 (CN), 127.8, 128.1, 128.4, 128.5, 129.8, 132.7, 132.8, 135.8 C (Ph), 168.8 (C=O), 171.4 (C=O), 198.0 (C=O). Anal. Calcd for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.53; H, 5.46; N, 4.13; **9a**, mp 37–39 °C (hexane); IR $\nu_{max}$ ($CHCl_3$): 1750 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): 2.39 (s, 3H, Me), 3.81 (s, 3H, MeO), 4.55 (s, 1H, $CH_2$=), 4.97 (s, 1H, $CH_2$=), 7.17–7.20 (m, 2H, H(Ar)), 7.46–7.55 (m, 5H, H(Ar)), 7.91–7.93 (m, 2H, H(Ar)); $^{13}C$ NMR (75 MHz, $CDCl_3$): 20.9 (Me), 51.5 (MeO), 94.4 ($CH_2$), 125.4, 127.8, 128.4, 128.7, 131.4, 133.1, 133.2, 138.1 (C(Ar)), 155.0 (C=), 158.4 (C=N), 164.9 (C=O). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.31; H, 6.35; N, 4.94; *cis*-**10a**, mp 156 °C (hexane–$CH_2Cl_2$); IR $\nu_{max}$ ($CHCl_3$): 1735 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): 2.49 (s, 3H, Me), 3.74 (s, 3H, MeO), 3.89 (s, 3H, MeO), 3.91 (d, 1H, $H^4$, $J = 17.4$), 4.43 (d, 1H, $H^4$, $J = 17.4$), 6.77–6.80 (m, 2H, H(Ar)), 6.91–6.98 (m, 3H, H(Ar)), 7.03–7.06 (m, 3H, H(Ar)), 7.33–7.41 (m, 4H, H(Ar)), 8.01–8.05 (m, 2H, H(Ar)); $^{13}C$ NMR (75 MHz, $CDCl_3$): 21.3 (Me), 48.2 $C^4$, 52.2 (MeO), 52.5 (MeO), 66.1 $C^3$, 91.1 $C^2$, 126.5, 126.6, 127.4, 127.9, 128.2, 129.1, 130.3, 137.3, 138.9, 141.9 C(Ar), 172.4, 173.8, 175.4 (2 C=O+C=N). Anal. Calcd for $C_{27}H_{25}NO_4$: C, 75.86; H, 5.89; N, 3.28. Found: C, C, 75.82; H, 5.97; N, 3.21; *trans*-**10a**, mp 159–160 °C (hexane–$CH_2Cl_2$); IR $\nu_{max}$ ($CHCl_3$): 1750, 1740 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): 2.46 (s, 3H, Me), 3.30 (s, 3H, MeO), 3.55 (s, 3H, MeO), 3.56 (d, 1H, $H^4$, $J = 16.7$), 4.28 (d, 1H, $H^4$, $J = 16.7$), 7.26–7.36 (m, 10H, H(Ar)), 7.45–7.48 (m, 2H, H(Ar)), 7.96–7.99 (m, 2H, H(Ar)); $^{13}C$ NMR (75 MHz, $CDCl_3$): 21.2 (Me), 49.0 C(4), 51.7 (MeO), 51.9 (MeO), 67.7 $C^3$, 91.4 $C^2$, 125.9, 126.5, 126.6, 127.2, 127.8, 127.9, 128.0, 129.0, 130.3, 136.9, 141.8, 142.3 C(Ar), 170.1, 171.9, 173.8 (2 C=O, C=N). Anal. Calcd for $C_{27}H_{25}NO_4$: C, 75.86; H, 5.89; N, 3.28. Found: C, 76.06; H, 6.03; N, 3.07.