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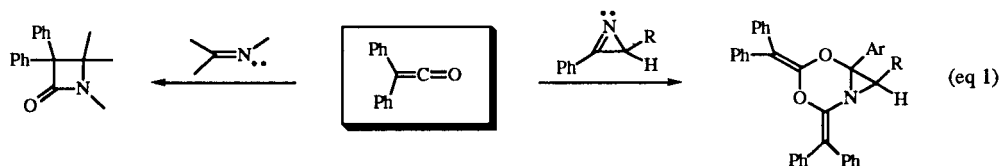
Received March 5, 1996

Revised September 13, 1996

2-Formyl-2*H*-azirine-*N*-arylimines **1a-c** react with diphenylketene **2** to afford 2*H*-2-aziriny-2-azetidiones **3a-c** and *N*-aryldiphenylacetamides **4a-c** by reaction at the exo-imine group. Derivatives containing the bulkier methyl group at the 2-position, **1d-f**, produce only **4a-c**.

J. Heterocyclic Chem., **34**, 341 (1997).

While simple imines afford 2-azetidiones upon reaction with diphenylketene [1], alkyl and aryl substituted 2*H*-azirines produce 2:1 adducts that are bicyclic aziridines [2,3] (eq 1).

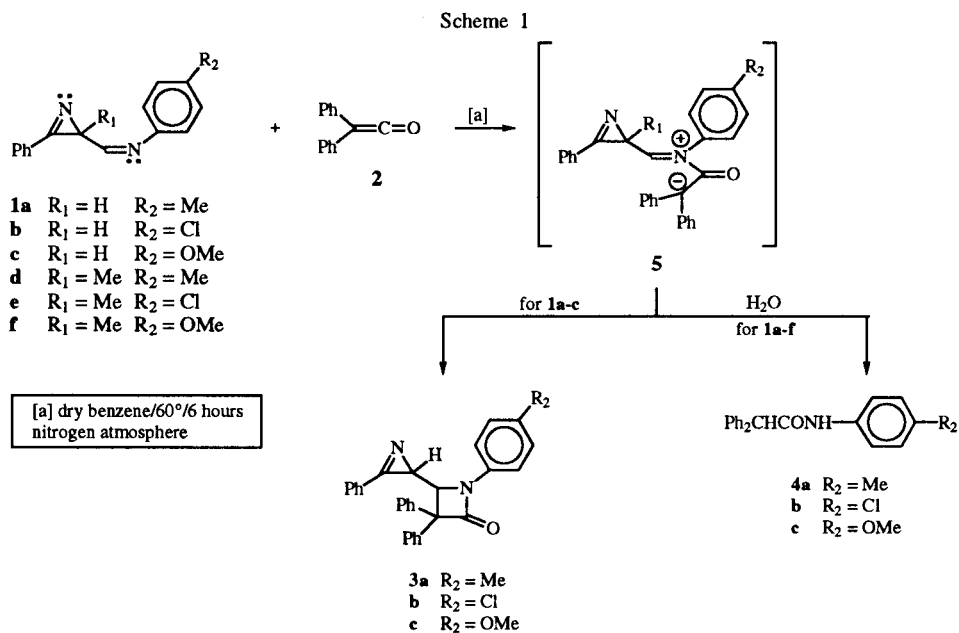


The ready availability of 2-formyl-2*H*-azirine-*N*-arylimines **1** [4,5], wherein both imine types are encountered, prompted us to investigate the behavior of **1** in the above reaction, with special emphasis on synthetic and mechanistic implications.

2-Formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1a-c** reacted smoothly with diphenylketene **2** (generated by thermal decomposition of diphenyldiazoethanone) in benzene (60°, 6 hours, nitrogen atmosphere) to afford 2*H*-2-aziriny-2-aze-

tidinones **3a-c** (35–41% yields, as a single diastereomer) and *N*-aryldiphenylacetamides **4a-c** (20% yield) (Scheme 1, Table I). The former showed characteristic carbonyl absorption in the ir spectra (ν 1750 cm^{-1}) and two CH doublets with

identical coupling constants values in the ^1H nmr spectra (corresponding to tetrahedral carbon units as determined by the chemical shifts in the ^{13}C nmr spectra). Formation of *N*-aryldiphenylacetamides **4a-c** may be attributed to the interception by intermediate **5** (Scheme 1) of trace quantities of water in the reaction medium, in competition with ring closure to **3**. The ^1H nmr spectra of the crude products revealed the presence of the corresponding 2-formyl-3-phenyl-2*H*-azirine, an observation consistent with initial



attack of water at the exo-imine for formation of *N*-aryldiphenylacetamides **4a-c**. Control experiments showed that 2-formyl-2*H*-azirine-*N*-arylimines **1** are stable under the reaction conditions in the absence of diphenylketene. Interestingly, reaction of 2-formyl-2-methyl-3-phenyl-2*H*-azirine-*N*-arylimines **1d-f** with diphenylketene **2** produced only *N*-aryldiphenylacetamides **4a-c** (40-55% yield, Table I) in spite of all efforts to exclude water. In this case, increased steric hindrance at the imine carbon favors reaction of **5** with the small water molecule. The possibility of **5** having survived the reaction conditions only to suffer subsequent hydrolysis at the work-up stage should not be discarded.

The results of the reactions of 2-formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1** with diphenylketene **2** demonstrate the enhanced reactivity of the exo-imine group, furnishing a convenient route to the previously unknown 2*H*-2-aziriny-2-azetidinone system in a highly diastereoselective fashion.

Table I

Yields (%) of the 2*H*-2-Aziriny-2-azetidinones **3** and *N*-Aryldiphenylacetamides **4** from Different 2-Formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1**

2-Formyl-3-phenyl-2 <i>H</i> -azirine- <i>N</i> -arylimines	2 <i>H</i> -2-Aziriny-2-azetidinones 3	<i>N</i> -Aryldiphenylacetamides 4
1a	3a (41)	4a (20)
1b	3b (40)	4b (22)
1c	3c (35)	4a (20)
1d	—	4a (55)
1e	—	4b (40)
1f	—	4c (51)

EXPERIMENTAL

General Procedure for the Synthesis of 2-Formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1**.

2-Formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1** were prepared by reaction of the appropriate aniline with either 2-formyl-3-phenyl-2*H*-azirine [**4**] (for **1a-c**) or 2-formyl-2-methyl-3-phenyl-2*H*-azirine [**6**] (for **1d-f**) using the reported procedure [4,5]. The 2-formyl-3-phenyl-2*H*-azirine-*N*-arylimines were obtained quantitatively as colorless oils and used without further purification. The ¹H nmr spectral data of previously unreported imines **1d-f** are as follows:

2-Formyl-2-methyl-3-phenyl-2*H*-azirine-*N*-(4-tolyl)imine (**1d**).

This compound had ¹H nmr (carbon tetrachloride): δ 1.65 (s, 3H), 2.28 (s, 3H), 6.40-8.00 (m, 10H).

2-Formyl-2-methyl-3-phenyl-2*H*-azirine-*N*-(4-chlorophenyl)imine (**1e**).

This compound had ¹H nmr (carbon tetrachloride): δ 1.65 (s, 3H), 6.40-8.00 (m, 10H).

2-Formyl-2-methyl-3-phenyl-2*H*-azirine-*N*-(4-anisyl)imine (**1f**).

This compound had ¹H nmr (carbon tetrachloride): δ 1.65 (s, 3H), 3.73 (s, 3H), 6.40-8.00 (m, 10H).

General Procedure for the Reaction of 2-Formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1a-f** with Diphenylketene (**2**).

All of these reactions were carried out under a nitrogen atmosphere. A solution containing 2-formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1a** (0.5 mmole) and diphenyldiazoethane (133.5 mg, 0.6 mmole) in dry benzene (5 ml) was heated at 60° for 6 hours. The solvent was removed in vacuum and the residue was separated by column chromatography (florisil) to give, from the reaction of 2-formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1a-c**, 2*H*-2-aziriny-2-azetidinones **3a-c** in 35-41% yield (benzene as eluant) and *N*-aryldiphenylacetamides **4a-c** in 20-22% yield (benzene-diethyl ether (90:10) as eluant), respectively (Table I).

From the reaction of 2-formyl-3-phenyl-2*H*-azirine-*N*-arylimines **1d-f** only *N*-aryldiphenylacetamides **4a-c** were obtained in 40-55% (Table I).

1-(4-Tolyl)-3,3-diphenyl-4-(3-phenyl-2*H*-2-aziriny)-2-azetidinone (**3a**).

This compound was obtained as a colorless solid from the reaction of 2-formyl-3-phenyl-2*H*-azirine-*N*-(4-tolyl)imine **1a**, mp 210-212°; ir (potassium bromide): ν 1754, 1515, 1488, 1388, 1372 cm⁻¹; ¹H nmr (deuteriochloroform): δ 7.55 (m, 19H), 4.11 (d, 1H, J = 8 Hz), 2.35 (s, 3H), 2.24 (d, 1H, J = 8 Hz); ¹³C nmr (deuteriochloroform): δ 167.1, 167.1, 140-119 (arom), 70.0, 69.7, 32.1, 21.0.

Anal. Calcd. for C₃₀H₂₄ON₂: C, 84.11; H, 5.61; N, 6.54. Found: C, 83.78; H, 5.24; N, 6.51.

4-Tolyldiphenylacetamide (**4a**).

This compound was obtained as a colorless solid from the reaction of 2-formyl-3-phenyl-2*H*-azirine-*N*-(4-tolyl)imine **1a** or 2-formyl-2-methyl-3-phenyl-2*H*-azirine-*N*-(4-tolyl)imine **1d**, mp 172-173°; lit [7] mp 172-174°.

1-(4-Chlorophenyl)-3,3-diphenyl-4-(3-phenyl-2*H*-2-aziriny)-2-azetidinone (**3b**).

This compound was obtained as a colorless solid from the reaction of 2-formyl-3-phenyl-2*H*-azirine-*N*-(4-chlorophenyl)imine **1b**, mp 204-206°; ir (potassium bromide): ν 1751, 1594, 1494, 1448, 1384 cm⁻¹; ¹H nmr (deuteriochloroform): δ 7.60 (m, 19H), 4.10 (d, 1H, J = 8 Hz), 2.21 (d, 1H, J = 8 Hz); ¹³C nmr (deuteriochloroform): δ 167.1, 166.7, 160-114 (arom), 70.2, 69.7, 31.8.

Anal. Calcd. for C₂₉H₂₁ClN₂O: C, 77.59; H, 4.68; N, 6.24; Found: C, 77.64; H, 4.36; N, 6.07.

4-Chlorophenyldiphenylacetamide (**4b**).

This compound was obtained as a colorless solid from the reaction of 2-formyl-3-phenyl-2*H*-azirine-*N*-(4-chlorophenyl)imine **1b** or 2-formyl-2-methyl-3-phenyl-2*H*-azirine-*N*-(4-chlorophenyl)imine **1e**, mp 198-199°; lit [8] mp 204°.

1-(4-Anisyl)-3,3-diphenyl-4-(3-phenyl-2*H*-2-aziriny)-2-azetidinone (**3c**).

This compound was obtained as a colorless solid from the reaction of 2-formyl-3-phenyl-2*H*-azirine-*N*-(4-anisyl)imine **1c**, mp 170-72°; ir (potassium bromide): ν 1745, 1513, 1448, 1391, 1299, 1247 cm⁻¹; ¹H nmr (deuteriochloroform): δ 7.59 (m, 19H), 4.68 (d, 1H, J = 8 Hz), 3.82 (s, 3H); 2.22 (d, 1H, J = 8 Hz), ¹³C nmr (deuteriochloroform): δ 166.8, 166.4, 156-114 (arom), 69.9, 55.5, 32.0.

Anal. Calcd. for C₃₀H₂₄N₂O₂: C, 81.08; H, 5.41; N, 6.31. Found: C, 80.83; H, 5.22; N, 6.27.

4-Anisylidiphenylacetamide (**4c**).

This compound was obtained as a colorless solid from the reaction of 2-formyl-3-phenyl-2*H*-azirine-*N*-(4-anisyl)imine **1c** or 2-formyl-2-methyl-3-phenyl-2*H*-azirine-*N*-(4-anisyl)imine **1f**, mp 187-188°; lit [9] mp 188-189°.

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