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Regiospecific Cycloaddition Reaction of 2-Aryl and 2-Alkyl 1-Arenesulfonylaziridines with Isocyanates Using Sodium Iodide

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Key Words: 2-aryl/alkyl; N-arenesulfonylaziridines; isocyanates; Sodium iodide; trisubstituted-2-imidazolidinones; regiospecific cycloaddition.

Abstract: *Reaction of title aziridines with isocyanates in presence of sodium iodide is regiospecific. 2-aryl N-sulfonylaziridines give the 1-N-arylsulfonyl-3-alkyl/aryl-4-phenyl-2-imidazolidinones exclusively whereas the 2-alkyl substituted aziridines afford only the 1-N-alkyl/aryl-3-N-arylsulfonyl-4-alkyl-2-imidazolidinones.*

Cycloaddition of monosubstituted oxiranes with isocyanates involving the use of several catalysts produced a variety of 2-oxazolidinones and the 3,5 - disubstituted derivatives are formed invariably[1] with a few exceptions[2]. The use of tetraphenyl-stibonium iodide selectively yields 3,4-disubstituted oxazolidinones[3].

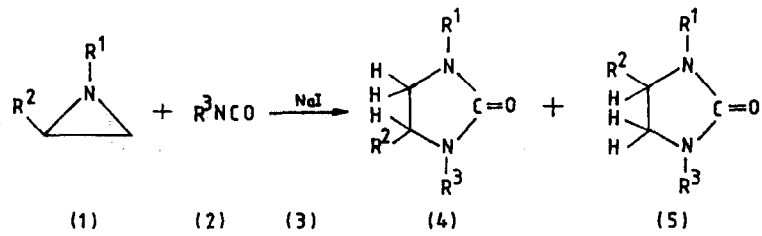
However, Cycloaddition of three membered nitrogen heterocyclic systems i.e. aziridines with isocyanates have been little investigated. To our knowledge only two such studies[4,5] on ring expansion reactions of arenesulfonylaziridines with isocyanates have been published. In both the cases 2,3-unsubstituted aziridines were subjected to reactions with isocyanates; no reactions between monosubstituted arenesulfonylaziridines and isocyanates have been reported so far.

Herein we report for the first time the regiospecific reaction between 1-arenesulfonyl-2-aryl and 2-alkyl aziridines with aryl and alkyl isocyanates. We have found that sodium iodide can act as a versatile catalyst under very mild conditions for the selective formation of **4** or **5**, depending on the nature of the starting aziridine.

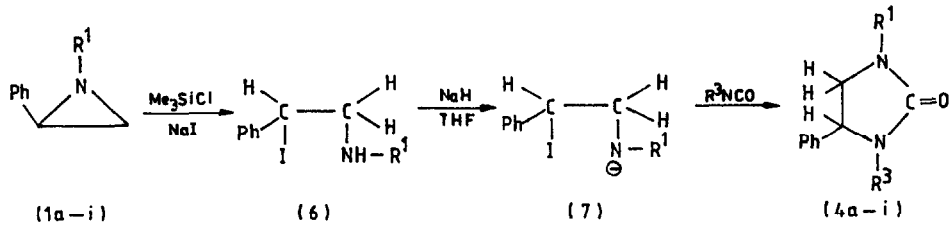
Interestingly, when 1-arenesulfonyl-2-arylaziridines were reacted with various isocyanates in presence of sodium iodide, 1-N-arylsulfonyl-3-alkyl/aryl-4-phenyl-2-imidazolidinones (**4**) were the only product formed whereas 1-arenesulfonyl-2-alkyl aziridine under identical reaction conditions gave exclusively the 1-N-alkyl/aryl-3-N-arylsulfonyl-4-alkyl-2-imidazolidinones (**5**). However, it was found that the nature of the isocyanate used does not affect the regiochemistry of the reaction but only alters the yields of the products. Reactions with aryl isocyanates generally afford better yields than those with alkyl isocyanates.

In both the cases the regiochemical structures of imidazolidinones (**4a-i**) and (**5j-l**) have been confirmed by comparing them with those synthesised by us independently following a route which would permit only the formation of **4a-i** (Scheme 2) and **5j-l** (Scheme 3). This was done by reacting ß-iodophenylethylarylsulfonamides (**6**) and 2-Arylsulfonamido propyliodides (**8**), the regiochemistry of which has been established by us previously[6], with NaH in dry tetrahydrofuran to generate the corresponding anions **7** and **9** which on addition of isocyanates would produce exclusively the imidazolidinones **4a-i** and **5j-l** respectively[7].

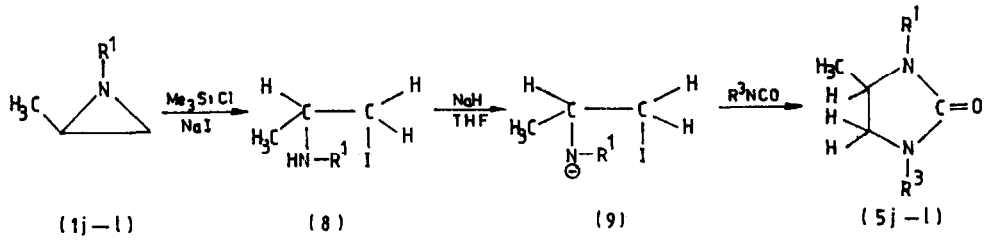
The regiospecificity of the reaction can be explained if it is assumed that attack of the iodide ion preceeds cycloaddition and such attack is governed by electronic rather than steric factors. Change in the regiochemistry of nucleophilic attack on aziridines as a consequence of change in substituents is well



Scheme 1



Scheme 2



Scheme 3

precedented[8].

In a typical procedure, to a solution of **1a** (.518 g, 2m mol) and **3** (.298 g, 2m mol) in dry tetrahydrofuran was added 2m mol (.238 g) of **2a** through a syringe at room temperature and stirred for 6h. The solvent was then evaporated, water added and the mixture extracted with benzene. The organic layer was washed first with 1%, $Na_2S_2O_3$(aq.) and then with water, followed by drying over anhydrous sodium sulfate. The solvent was evaporated and the resultant mixture was subjected to silica gel column chromatography (eluted with benzene: hexane 95:5) to afford **4a** in 98% yield.

Reaction conditions and results are summarised in Table 1.

Table 1

Entry	R^1	R^2	R^3	Yield (%) (4 or 5)	Time (hours)
4a	$-SO_2C_6H_5$	-Ph	-Ph	98.0	6
4b	$-SO_2C_6H_4CH_3$	-Ph	-Ph	92.9	6
4c	$-SO_2C_6H_4Cl$	-Ph	-Ph	94.8	6
4d	$-SO_2C_6H_5$	-Ph	$-CH_2CH_2CH_3$	76.0	18
4e	$-SO_2C_6H_4CH_3$	-Ph	$-CH_2CH_2CH_3$	69.0	18
4f	$-SO_2C_6H_4Cl$	-Ph	$-CH_2CH_2CH_3$	78.0	18
4g	$-SO_2C_6H_5$	-Ph	$-C(CH_3)_3$	51.0	18
4h	$-SO_2C_6H_4CH_3$	-Ph	$-C(CH_3)_3$	49.0	18
4i	$-SO_2C_6H_4Cl$	-Ph	$-C(CH_3)_3$	46.0	18
5j	$-SO_2C_6H_4CH_3$	$-CH_3$	-Ph	46.0	18
5k	$-SO_2C_6H_5$	$-CH_3$	$-CH_2CH_2CH_3$	31.0	18
5l	$-SO_2C_6H_5$	$-CH_3$	$-C(CH_3)_3$	33.0	18

References and Notes

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7. Regiochemical structure of compounds **4a-i** and **5j-l** were established by comparing the m.p values as well as the IR and NMR spectra obtained from authentic imidazolidinones prepared by alternate procedure depicted in Scheme 2 and Scheme 3 respectively.

   All these compounds are unknown but gave satisfactory NMR, mass measurements and elemental analysis data. The NMR spectra of selected compounds are given below.

   4a: ^{1}HNMR ($CDCl_3$, 100MHz): δ = 3.82 (dd,1H, J ~ 5Hz,9Hz), 4.34 (t,1H, J ~ 9Hz). 5.24 (dd, 1H, J ~ 5Hz, 9Hz), 7.32-7.48 (m,15H) ^{13}CNMR ($CDCl_3$, 25 MHz): δ = 49.8, 57.8, 128.8, 132.0, 132.8, 134.4, 136.2, 137.0, 141.8

   4d: ^{1}HNMR ($CDCl_3$, 100 MHz): δ = 0.742 (t,3H), 1.652 (m,2H); 2.576 (m, 2H), 3.711 (dd, 1H, J ~ 6 Hz, 10 Hz), 4.213 (t,1H, J ~ 10 Hz), 4.760 (dd, 1H,J ~ 6 Hz, 10 Hz), 7.137-7.287 (m, 10H).

   ^{13}CNMR ($CDCl_3$, 25 MHz): δ = 10.6, 19.4, 43.4, 50.6, 56.2, 128.6, 130.1, 134.6, 138.6, 142.0

   4g: ^{1}HNMR ($CDCl_3$, 100 MHz): δ = 1.218 (s, 9H), 3.688 (dd, 1H, J ~ 2Hz, 9Hz), 4.095 (t, 1H, J ~ 9Hz), 4.740 (dd, 1H, J ~ 2Hz, 9Hz), 7.289-7.341 (m,10H).

   ^{13}C NMR ($CDCl_3$, 25 MHz): δ = 27.4, 50.6, 60.0, 125.8, 128.2, 129, 130.2, 133.8, 142.6.

   5j: ^{1}HNMR ($CDCl_3$, 100 MHz): δ = 1.625 (d,3H, J ~ 6Hz), 2.40 (S,3H), 3.446(dd,1H, J ~ 4Hz, 9Hz), 4.115 (t,1H, J ~ 9Hz), 4.45 (m, 1H), 7.24-7.38 (m,9H).

   ^{13}C NMR ($CDCl_3$, 25MHz): δ = 21.0, 22.2, 49.8, 50.2, 119.00, 127.0, 131.2, 132.0, 132.8, 148.0.
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