Phase-Transfer Catalyzed Synthesis of 1,2-Disubstituted Aziridines from Sulfuranes and Schiff Bases or Aldehyde Arylhydrazones

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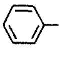
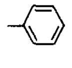
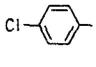
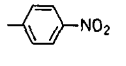
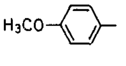
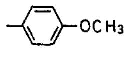
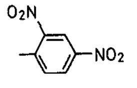
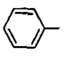
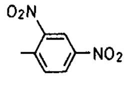
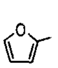
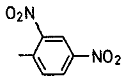
There are several reports on phase-transfer catalyzed two-phase reactions[1] in which anionic reactants are transferred from an aqueous to an organic phase by quaternary ammonium salts[2,3,4], for example, cycloadditions[2,3,5] and insertion reactions[6] of halocarbenes produced with aqueous sodium hydroxide. Utilizing the fact that methylenedimethylsulfurane is a methylene-transfer agent[7] which can add a methylene group to a C=C double bond, we elaborated a new synthesis of 1,2-disubstituted aziridines (**4, 5**) which involves the phase-transfer catalyzed production of methylenedimethylsulfurane from trimethylsulfonium iodide (**1**) in aqueous sodium hydroxide and its interaction with *N*-arylbenzaldimines (Schiff bases, **2**) or aldehyde arylhydrazones (**3**).

Table. 1,2-Disubstituted Aziridines (**4**, **5**) prepared

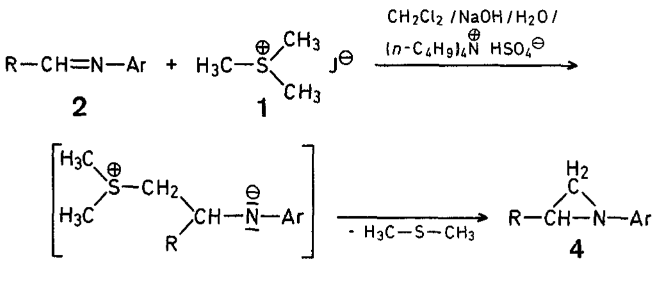
Educt	R	Ar	Product	Yield [%]	b.p./torr or m.p.[a] [°C] (solvent)	Molecular Formula[b]	I.R. (KBr)[c] ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$/TMS$_{int}$)[d] δ [ppm]
2a			**4a**	94	b.p. 120°/0.05	—	2980 (ArH stretching); 1620 (C=C)	2.2 (m, 2H, CH$_2$); 2.95 (q, 1H, 2-H); 6.8–7.45 (m, 10H$_{arom}$)
2b			**4b**	80	m.p. 155–156° (benzene/pet. ether)	$C_{14}H_{11}ClN_2O_2$ (274.7)	2950 (ArH stretching); 1600 (C=C); 1325; 1310 (NO$_2$)	
2c			**4c**	84	m.p. 159–160° (benzene/pet. ether)	$C_{16}H_{17}NO_2$ (255.3)		2.2 (m, 2H, CH$_2$); 2.40 (q, 1H, 2-H); 3.75 (s, 6H, 2OCH$_3$); 6.6–7.4 (m, 8H$_{arom}$)
3a	H_3C-		**5a**	92	m.p. 130–132° (benzene/pet. ether)	$C_9H_{10}N_4O_4$ (238.2)	3200 (ArH stretching); 1595 (C=C); 1510; 1300 (NO$_2$); 1600 (NH bending)	
3b			**5b**	87	m.p. 194–195° (chloroform/benzene)	$C_{14}H_{12}N_2O_4$ (272.3)		1.63 (m, 2H, CH$_2$); 2.64 (q, 1H, 2-H); 6.62–8.1 (m, 8H$_{arom}$); 8.21 (s, 1H, NH)
3c			**5c**	81	m.p. 143–145° (benzene/pet. ether)	$C_{12}H_{10}N_4O_5$ (290.2)		1.6 (m, 2H, CH$_2$); 2.6 (q, 1H, 2-H); 5.5–6.8 (m, 3H$_{furyl}$); 7.0–7.8 (m, 3H$_{arom}$); 7.95 (s, 1H, NH)

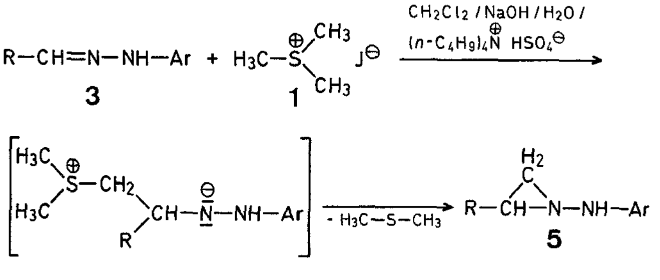
[a] Melting points were determined using a Gallenkamp apparatus and are uncorrected.

[b] The microanalyses were in satisfactory agreement with the calculated values.

[c] Recorded on a Perkin Elmer Infracord instrument.

[d] Recorded on Varian A-60 Spectrometer.





The mechanism of the reaction presumably involves nucleophilic attack of the *in situ* generated methylenedimethylsulfurane on the imine function of **2** or **3** followed by displacement of the dimethylsulfonio group (which is an excellent leaving group) by the azene anion to form the aziridine **4** or **5**, respectively. The possibility of trimethylsulfonium ion to act as a phase-transfer catalyst in the reaction is ruled out because of the small size of the methyl group; thus, the reaction does not proceed in the absence of the ammonium salt under otherwise identical conditions whereas in the presence of 1–5 mol% of tetrabutylammonium hydrogen sulfate the aziridines **3** or **4** are obtained in good yields. Conventional methods[8,9,10] are inappropriate for the synthesis of these aziridines.

The structures of the compounds **4** and **5** were established by microanalyses, physical and spectral data and all compounds except **4a** are new.

1,2-Disubstituted Aziridines (4, 5); General Procedure:

The imine **2** or hydrazone **3** (0.1 mol) and tetrabutylammonium hydrogen sulfate (0.5 g, 1.35 mol) are dissolved in dichloromethane (100 ml) and a layer of 50% aqueous sodium hydroxide is introduced underneath this solution. Trimethylsulfonium iodide (**1**; 20.4 g, 0.1 mol) is then added and the whole is warmed at 50 °C with vigorous stirring for 2 h, whereupon the originally undissolved sulfonium salt disappears. The mixture is next poured onto ice, and the organic phase is separated, washed with water, and dried. The solvent is evaporated and the residual product **4** or **5** distilled in vacuo.

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