Aziridines; III[1]. 1,2,3-Trisubstituted Aziridines by the Reaction of Phenyldiazomethane with Imines in the Presence of Zinc Iodide

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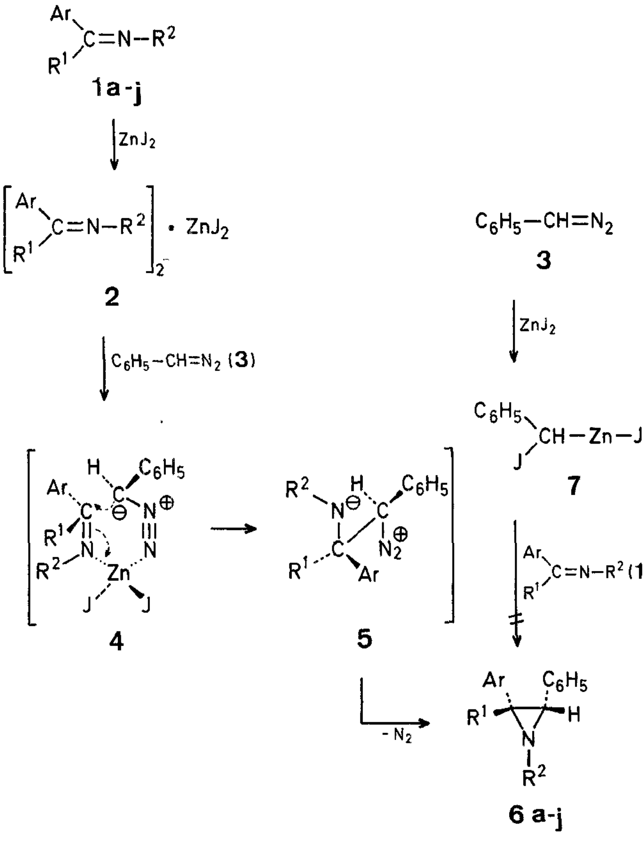
Previously we have found that reactions of phenyldiazomethane (**3**) with aromatic aldehydes in the presence of zinc iodide yielded desoxybenzoin derivatives[2]. In this paper, we present the results of our study on the reactions of **3** with *N*-arylideneamines **1** in the presence of zinc iodide. *N*-Substituted 2-aryl-3-phenylaziridines **6** were found to be the products (Table). The ^{1}H-N.M.R. spectra of crude reaction mixtures showed that *cis*-aziridines were formed exclusively. The prod-



ucts were detected and identified by spectral methods and by comparison with original samples obtained by other methods[1,3,4,5].

The mechanism of the present reaction differs significantly from that of the typical cyclopropanation[6] of olefins using phenyldiazomethane involving the zinc carbenoid **7**. However, compound **7**, obtained by the decomposition of phenyldiazomethane (**3**) in the presence of zinc iodide, did not show reactivity towards **1a**. Probably aziridines **6** are produced by the nucleophilic attack of phenyldiazomethane (**3**) on imines **1** in which the C=N bond is activated by the imine/zinc iodide complex (**2**) formation. When zinc iodide was added to an ether solution of imines **1**, the complexes **2** precipitate in the form of colourless solids. Addition of phenyldiazomethane (**3**) to the solution of a complex **2** containing excess of imine **1**, causes the evolution of nitrogen and formation of aziridine **6**.

The proposed mechanism of the reaction is in good agreement with previous reports on the addition of aliphatic diazo compounds to activated imines bearing electronegative substituents which can polarize the C=N bond[7,8].

Zinc iodide seems to be the catalyst of choice. Replacement of it by other catalysts [copper(I) bromide, copper(II) acetylacetonate, copper dust or Moser complex] results in the formation of imidazolidine derivatives by an azomethine ylid mechanism[9]. Attempts to obtain other aziridine derivatives using aliphatic diazocompounds (e.g. diazomethane, ethyl diazoacetate, diazoacetonitrile, or dimethyl diazomalonate) were unsuccessful.

cis-N-Substituted-2,3-diarylaziridines 6; General Procedure:

To a magnetically stirred solution containing imine **1** (0.25 mol) in ether (50 ml) [or a mixture of ether/acetonitrile (3 : 1) for **1h**] a mixture of zinc iodide (1.6 g, 5 mmol) in ether (10 ml) is added. To this mixture, under nitrogen at room temperature, a solution of phenyldiazomethane (**3**; 1.2 g, 10 mmol) in ether (15 ml) is added dropwise. Each portion is added only after the colour of the diazo compound has disappeared. The mixture is stirred for an additional 30 min, filtered, and extracted with 5% ammonium hydroxide solution (50 ml) to remove the zinc iodide. The organic phase is dried with magnesium sulphate and evaporated. Excess of imine **1** is distilled off under reduced pressure or separated by fractional crystallisation from ethanol (**1g** and **1h**). The residue is analysed by ^{1}H-N.M.R., and then purified on a column of neutral aluminium oxide (hexane/ether). Crude aziridines **6** are purified by additional chromatography (**6a–c**) or by crystallisation (hexane for **6d, f, i, j** or methanol for **6e, g, h**).

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Table. *cis-N*-Substituted-2,3-diarylaziridines **6**

Product	Ar	R^1	R^2	Yield[a] [%]	m.p. or b.p./torr	Molecular formula[c] or Lit. Data	M.S.[d] *m/e*	^{1}H-N.M.R. (CCl_4)[e,f] δ [ppm]
6a	C_6H_5	H	CH_3	50	oil[b]	112–114°/ 0.2[1]	209 (M^+), 208 (100%)	2.57 (s, 3H); 2.62 (s, 2H); 6.9–7.2 (m, 10H)
6b	4-H_3C—C_6H_4	H	CH_3	47	oil[b]	$C_{16}H_{17}N$ (223.3)	223 (M^+), 222 (100%)	2.10 (s, 3H); 2.60 (s, 3H); 2.61 (s, 2H); 6.7–7.1 (m, 9H)
6c	4-H_3CO—C_6H_4	H	CH_3	43	oil[b]	$C_{16}H_{17}NO$ (239.2)	239 (M^+), 224 (100%)	2.57 (s, 3H); 2.60 (s, 2H); 3.50 (s, 3H); 6.4–7.1 (m, 9H)
6d	C_6H_5	H	C_2H_5	37	74–75°	75–76°[4]	223 (M^+), 194 (100%)	1.2 (t, 3H, $J=7$ Hz); 2.55 (q, 2H, $J=7$ Hz); 2.65 (s, 2H); 6.9–7.2 (m, 10H)
6e	C_6H_5	H	*i*-C_3H_7	23	48–49°	$C_{17}H_{19}N$ (237.3)	237 (M^+), 194 (100%)	1.20 (d, 6H, $J=7$ Hz); 1.9 (m, 1H); 2.75 (s, 2H); 6.9–7.15 (m, 10H)
6f	C_6H_5	H	*t*-C_4H_9	15	92–93°	$C_{18}H_{21}N$ (251.3)	251 (M^+), 194 (100%)	1.10 (s, 9H); 3.05 (s, 2H); 7.0–7.2 (m, 10H)
6g	C_6H_5	H	C_6H_5	74	99–100°	99°[3]	271 (M^+), 270 (100%)	3.50 (s, 2H); 6.85–7.3 (m, 15H)
6h	C_6H_5	H	4-H_3CO—C_6H_4	68	68–69°	$C_{21}H_{19}NO$ (301.4)	301 (M^+), 197 (100%)	3.45 (s, 2H); 3.65 (s, 3H); 6.6–7.2 (m, 14H)
6i	C_6H_5	CH_3	CH_3	12	56–57°	$C_{16}H_{17}N$ (223.3)	223 (M^+), 222 (100)	1.55 (s, 3H); 2.48 (s, 1H); 2.60 (s, 3H); 6.7–7.4 (m, 10H)
6j[g]	C_6H_5	CH_3	C_2H_5	9	61–62°	$C_{17}H_{19}N$ (237.3)	237 (M^+), 236 (100%)	1.30 (t, 3H, $J=7$ Hz); 1.60 (s, 3H); 2.52 (s, 1H); 2.80 (q, 2H, $J=7$ Hz); 6.8–7.2 (m, 10H)

[a] Calculated on the crude phenyldiazomethane from ^{1}H-N.M.R. spectra using toluene as an internal concentration standard.

[b] Isolated and purified chromatographically on the column (see experimental).

[c] The microanalyses were in satisfactory agreement with the calculated values: C ±0.43, H ±0.3, N ±0.27.

[d] Mass spectra (70 eV) were obtained on LKB GCMS 2091 spectrometer.

[e] Measured with a Tesla 487 (80 MHz) spectrometer with TMS as an internal standard.

[f] Because of symmetry, ring protons of *N*-substituted 2,3-diphenylaziridines give a singlet, which is shifted 0.3–0.6 ppm to higher field in the *trans*-isomer[4,5].

[g] Prepared also by the ethylation of *cis*-2-methyl-2,3-diphenylaziridine[10] using triethyloxonium tetrafluoroborate.