Azines from *erythro*-1,2-Diaryl-2-(2-tosylhydrazino)-ethan-1-ol Derivatives by Acid Treatment

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In a previous paper[2], we have reported a procedure for the stereoselective reduction of tosylhydrazones of benzoin and desoxybenzoin derivatives by treatment with sodium cyanoborohydride in acidic media. The exclusive formation of the *erythro* diastereomers of *N*-aralkyl-*N'*-tosylhydrazines was observed when the asymmetric center in the starting material carried a group capable of complexation with the organometallic reagents.

Continuing our studies on such systems, we observed that the *erythro*-1,2-diaryl-2-(2-tosylhydrazino)-ethan-1-ol derivatives **1** produce the azines **4** in high yield when treated with formic acid in dichloromethane at room temperature (Table).

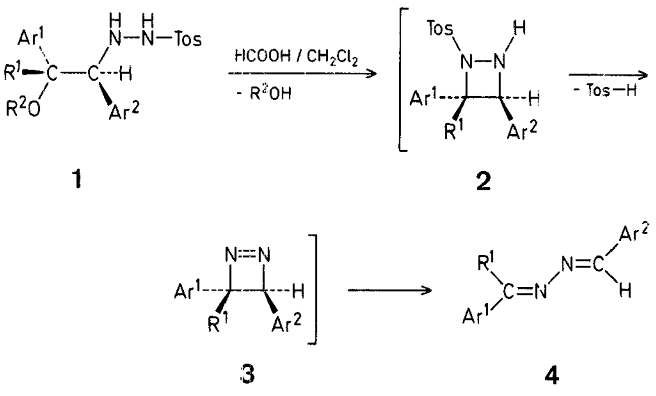

Table. Azines **4a-f** prepared

Substrate No.	Ar¹	Ar²	R¹	R²	Product	Yield [%]ᵃ	m.p. [°C]	Molecular formulaᵇ or Lit. m.p. [°C]	¹H-N.M.R. (CDCl₃/TMS) δ [ppm]
1a	C_6H_5	C_6H_5	H	H	**4a**	99	93-94°	93°[6]	7.35-8.05 (m, 10H); 8.72 (s, 2H)
1a′	C_6H_5	C_6H_5	H	CH_3	**4a**	99			
1a″	C_6H_5	C_6H_5	H	C_2H_5	**4a**	99			
1b	C_6H_5	4-H_3C—C_6H_4	H	H	**4b**	75	115-116°	112°[7]	2.42 (s, 3H); 7.15-8.0 (m, 9H); 8.63 (s, 1H); 8.66 (s, 1H)
1c	4-H_3CO—C_6H_4	C_6H_5	H	H	**4c**	85	85-86°	82-83°[8]	2.45 (s, 3H); 7.3-8.0 (m, 9H); 8.67 (s, 1H); 8.69 (s, 1H)
1d	4-H_3C—C_6H_4	4-H_3C—C_6H_4	H	H	**4d**	67	154-155°	154-155°[9]	2.40 (s, 6H); 7.15-7.85 (A_2B_2, 8H, J=8.0 Hz); 8.65 (s, 2H)
1e	4-H_3CO—C_6H_4	4-H_3CO—C_6H_4	H	H	**4e**	88	163-165°	168°[8]	2.45 (s, 6H); 7.3-7.85 (A_2B_2, 8H, J=8.0 Hz); 8.70 (s, 2H)
1f	C_6H_5	C_6H_5	CH_3	CH_3	**4f**	58	68-70°	$C_{15}H_{14}N_2$ (222.3)	2.30 (s, 3H); 7.3-8.05 (m, 10H); 8.71 (s, 1H)

ᵃ Yield of pure isolated product.

ᵇ Satisfactory microanalysis obtained: C +0.13, H +0.7, N −0.21; analysis performed on a Hewlett-Packard C,H,N Analyzer Model 185.

Although, our attempts to isolate any intermediates were unsuccessful, it seems likely that the four-membered species **2**, **3** and/or their protonated forms are involved in the formation of the products **4**.

In general, azines are synthesized by reaction of carbonyl compounds with hydrazine or hydrazones, but only symmetrical compounds are easily obtained in this manner[3]. More complex procedures are known for the synthesis of unsymmetrical azines[4]. Recently, a new method based on the alkylidene group exchange between azines and imines has been recommended for the synthesis of unsymmetrical azines[5]. In spite of being an indirect route, we expect that our method represents a valuable additional access to azines starting from benzoin derivatives.

Melting points are uncorrected and were determined with a Büchi apparatus; I.R. spectra were measured on a Perkin-Elmer 257 spectrometer; ¹H-N.M.R. spectra were recorded on a Varian spectrometer using TMS as internal standard. Carbonyl tosylhydrazones and *N*-aralkyl-*N*′-tosylhydrazines **1a-f** were prepared as previously described[2].

N-(1,2-diphenyl-2-methoxy)-propane-N′-tosylhydrazine (1f):
This product is prepared by cyanoborohydride reduction of 2-phenyl-2-methoxypropiophenone tosylhydrazone according to a previously described method[2]; yield: 93%; m.p. 119-120°C.

$C_{23}H_{26}N_2O_3S$	calc.	C 67.64	H 5.92	N 6.86
(410.45)	found	67.55	5.73	6.88

I.R. (KBr): ν=3245, 3210, 1345, 1155 cm⁻¹.

¹H-N.M.R. (CDCl₃/TMS): δ=1.60 (s, 3H); 2.50 (s, 3H); 3.10 (s, 3H); 3.60 (s, 1H); 4.30 (br. s, 1H); 6.8-7.7 ppm (m, 14H_{arom}).

Azines 4a-f; General Procedure:
N-Aralkyl-*N*′-tosylhydrazines **1a-f** (5.0 mmol) are dissolved in a 10 molar solution of formic acid in dichloromethane (10 ml). The solution is allowed to stand at room temperature for 24 h and then diethyl ether (50 ml) was added. The resulting solution is washed water (3 × 20 ml) and saturated aqueous sodium hydrogen carbonate solution (2 × 20 ml). The solvent is removed under reduced pressure to give crude products, successively purified by column chromatography on silica gel with benzene as eluent.

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